Chapter 6

Influence of Microscale Heterogeneous Bands on the Bulk Dynamic Response of VACNT Foams[5]

We describe the influence of microscale heterogeneous bands—with high-density (stiff) and low-density (compliant) regions—on the bulk dynamic response and the fundamental deformation mechanisms of the VACNT foams. These heterogeneous bands are synthesized by controlling the flow-rate of the feedstock during synthesis and thereby the microstructure of the VACNTs. We show that the banded VACNT foams exhibit a stress-strain response that is distinctively different from the VACNT foams with no heterogeneous bands. Specifically, we observe a significant stress plateau at low strains and a deformation-arrest characteristic of the soft middle band. Both of these features are desirable for impact and energy absorption applications. Using *in-situ* high-speed microscopy we observed that the samples exhibit different deformation mechanisms in dynamics compared to responses observed previously in quasistatic compression.

6.1 Introduction

Vertically aligned carbon nanotube (VACNT) foams present interesting mechanical characteristics due to their functionally graded properties, which arise from variations in CNT diameter [186], density [42,187], alignment [97], defect density [188] and the presence of contaminants [189]. Several synthesis methods have been developed over the last few years to control these parameters across different length scales and affect the nano, micro and macro-structures of the CNT foams to ultimately tailor the bulk mechanical properties in desired ways [23,31,73,190]. When compressed, the VACNT foams undergo strain localization and characteristic sequential buckling in which the buckles nucleate at the bottom low-density region of the sample, and sequentially progress one after the other, governed by their intrinsic functional property gradient

[5] This work was performed in collaboration with J. R. Raney, who synthesized the samples and supported the study.

[37,145]. Buckles always form fully before the next one forms, resulting in the remaining section of the sample showing no apparent deformation [123,145]. Such a controlled deformation is generally difficult to achieve in other macroscale materials, but a desirable characteristic for the design of protective materials against impact and vibration [191].

VACNT arrays with microscale heterogeneities have been synthesized previously [97,192,193] for energy dissipative applications. In a previous study, Raney et al. have examined the role of these microscale heterogeneities in tailoring the location and extent of strain localization during quasistatic loading and in changing the energy dissipation in low energy impact [193]. In this chapter, we examine the influence of microscale heterogeneities in the bulk dynamic response of VACNT arrays. We also demonstrate rate effects on the fundamental deformation mechanisms in the presence of the microscale heterogeneities.

6.2 Experimental methods

We synthesized the VACNT foams with microscale heterogeneities using a floating catalyst thermal chemical vapor deposition (tCVD) process as described in Section 2.1.1. The feedstock solution composed of carbon source and catalyst precursor was injected at controlled rates using a syringe-pump system and the input-rate was varied to cause heterogeneity in the microstructure during synthesis. Faster input-rates of the feedstock solution for a short duration results in growth of low-density regions in the sample [193]. It has been observed that the faster input rates have resulted in lower diameter CNTs compared to the normal rate of 0.8 ml min^{-1} (~30 nm in high input-rate and ~43 nm in normal input-rate), and more aligned CNT fibers [193]. We synthesized two kinds of samples with the middle soft band synthesized at 5 ml min^{-1} feedstock input rate for (i) 2 minutes, and (ii) 6 minutes. The two sections at the bottom and top of the sample were synthesized at the usual feedstock input rate of 0.8 ml min^{-1}. It should be noted that even though the top and bottom bands are synthesized under the same conditions, the bottom section grown after the soft middle band shows lower density and more aligned CNTs compared to the stiffest top band. All the samples were synthesized to a nominal height of 1 mm, and have a bulk density of 0.31±0.01 g cm^{-3} on average. A set of SEM images showing the microstructure of a VACNT foam with one soft middle band is given in Figure 6.1. We extracted the standalone VACNT samples, for the mechanical characterizations from the substrate using a razor blade.

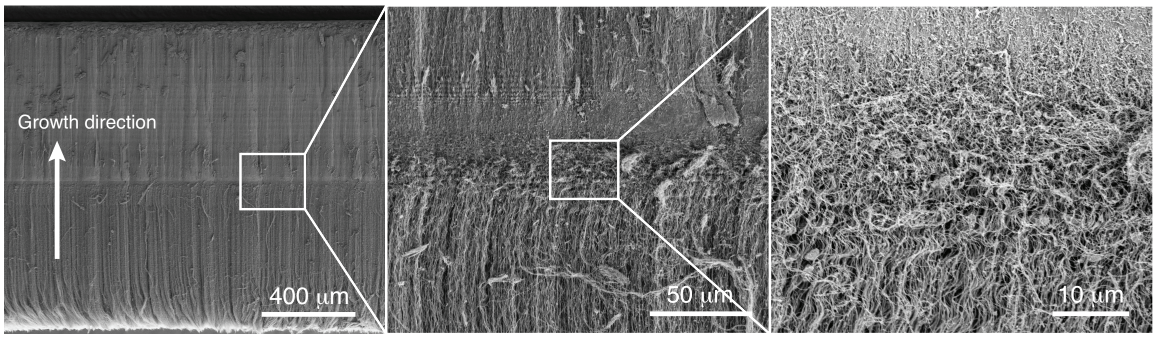

Figure 6.1. Microstructure of the VACNT foam with one middle soft band. The magnified view on the right shows the transition region from the stiff to soft band.

We performed striker impacts at controlled velocities between 0.5 and 7 m s^{-1} to evaluate the mechanical response of the samples. The standalone samples (extracted from substrate) were attached to a flat-plunge striker (7.2 g mass) and allowed to directly impact the impact force sensor mounted rigidly on a steel block. We measured the dynamic deformation using a geometric moiré interferometer and used a high-speed microscope synchronized with the rest of the experimental setup to visualize *in-situ* and characterize the complex microscale dynamic deformations. The displacement and force–time histories were then used to calculate the dynamic stress-strain response. The complete description of the experimental setup and the data reduction methodologies can be found in Section 2.4. We also performed quasistatic compression tests on an *Instron ElectroPulse E3000* compression testing system (see Section 2.3), to study the deformation mechanisms in comparison with the dynamic response.

6.3 Results and discussions

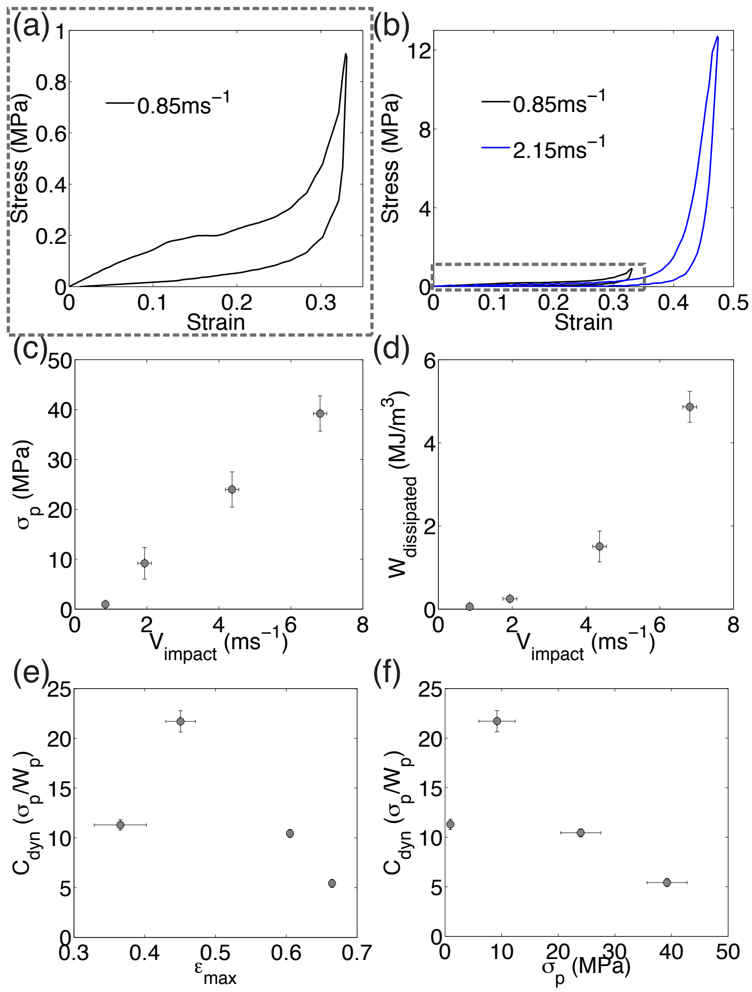

Figure 6.2. Dynamic response of VACNT foams with heterogeneous bands (with one soft middle band): **(a)** the stress-strain response of a sample impacted at 1.85 m s^{-1}, **(b)** the stress-strain response of a sample impacted at 2.15 m s^{-1} compared to the low-velocity impact response in (a), **(c)** the variation of peak stress with impact velocity, **(d)** the variation of hysteretic energy dissipated with impact velocity, and the variation of dynamic cushion factor with **(e)** maximum strain and **(f)** peak stress. The error bars represent the standard deviation of different samples tested.

When a VACNT foam sample with a middle soft band is impacted with a low velocity impact (<2 m s^{-1}), initially the stress rises linearly and then follows on to a plateau regime compressing the sample at very low stress levels (~0.2 MPa) and finally reaches densification of the soft bands, beyond which the stress rises rapidly (Figure 6.2 (a)). Here, the densification strain is approximately equal to the height of the bottom band normalized by the height of the sample. When a sample is impacted at higher velocities (>2 m s^{-1}), the initial low-stress levels continue up to the compression and densification of the stiff bottom and the soft middle bands followed by a rapid increase above 10 MPa without significant deformation (strain < 0.1) (Figure 6.2 (b)). Such a response follows for very high impact velocities up to 7 m s^{-1}.

We plotted the peak stress attained during impact and the energy dissipated through the loading-unloading hysteresis with increasing impact velocity (Figure 6.2 (c), (d)). Both the peak stress and the hysteretic energy dissipation increase with the increasing impact velocity. To evaluate the impact performance, we calculated the dynamic cushion factor—the peak stress normalized by the energy absorbed up to the peak stress—and plotted it against the varying maximum strain reached during impact (Figure 6.2 (e)). The trend in cushion factor for our samples is unique compared to conventional foam materials [147]. The cushion factor is very low for low velocity impacts and then exhibits a sharp rise above a certain impact velocity (~2 m s^{-1}), followed by a decreasing trend similar to that of other foam materials. This response arises due to the heterogeneous bands in the VACNT foams, where only the soft bands deform during the low velocity impacts, exhibiting low-cushion factors. It shows a sudden increase when the soft bands are compressed beyond their densification strain. It should be noted that the cushion factors calculated from quasistatic stress-strain curves are plotted against the peak stress, in general [147]. A similar cushion factor curve with peak stress in dynamics is given in Figure 6.2 (f).

We compared these dynamic responses of VACNT foams with heterogeneous bands to the responses of continuous VACNT foams (without any heterogeneous bands) of comparable bulk densities [166]. As shown in Figure 6.3 (a), both these foams exhibit similar peak stresses for a given impact velocity. The continuous VACNT foams dissipate higher energy through hysteresis in an intermediate velocity range between 2 m s^{-1} and 6 m s^{-1} and the energy dissipation is comparable for both foams bellow and above this range of velocities (Figure 6.3 (b)). This response leads to a better dynamic cushion factor for the continuous VACNT foams in the velocity range 2-6 m s^{-1} (Figure 6.3 (c), (d)). The lower the cushion factor, better the damping is since higher energy dissipation and lower transmitted stress amplitude both result in lower cushion factor.

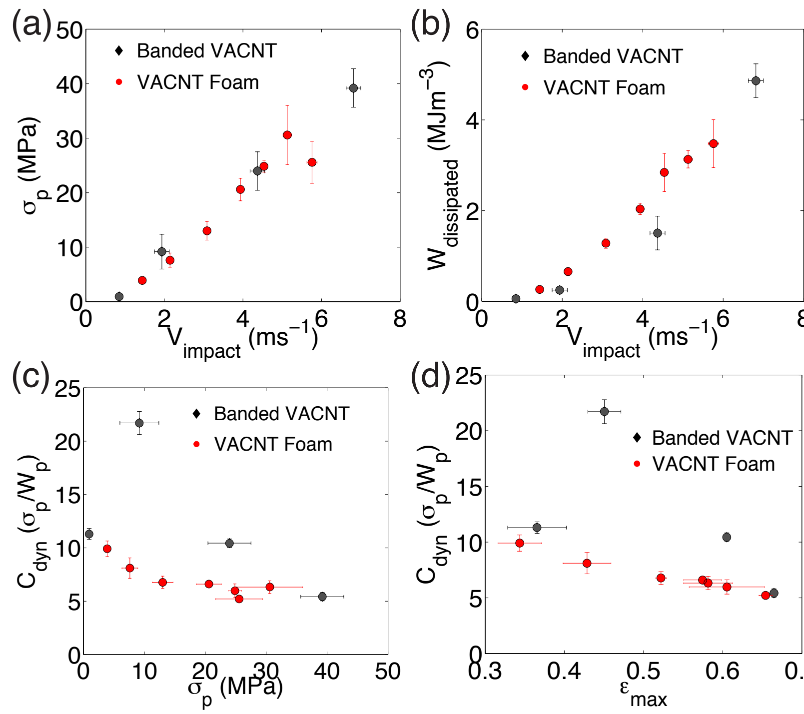

Figure 6.3. Comparison of dynamic response between VACNT foams with heterogeneous bands (banded VACNT) and VACNT foams without heterogeneous bands (VACNT foam): **(a)** the variation of peak stress with impact velocity, **(b)** the variation of hysteretic energy dissipated with impact velocity, and the variation of dynamic cushion factor with **(c)** maximum strain and **(d)** peak stress. The error bars represent the standard deviation of different samples tested.

To understand the effect of the thickness of the soft band on the fundamental dynamic response of the VACNT foams with heterogeneous bands, we characterized the dynamic response of samples with the middle soft band, synthesized for 2 min and 6 min, at similar impact velocities. An increased duration of the higher precursor input rate results in a large soft middle band and more gradual variation in the microstructure. We also used the response of continuous VACNT foams with no heterogeneous bands for benchmark reference. The VACNT foams with large soft bands exhibit a response that is more similar to the response of the VACNT foams with no heterogeneous bands. Also they exhibit significantly lower peak stresses compared to the VACNT foam with thin soft band. This response may be a result of gradual variation in the microstructure from the soft band to the band synthesized after the soft band, rather than the abrupt changes that could have been induced during the short feedstock input (2 min). The VACNT foams with thin soft bands exhibit a large plateau regime at very low stress levels, which are desirable for low-velocity impact protection applications.

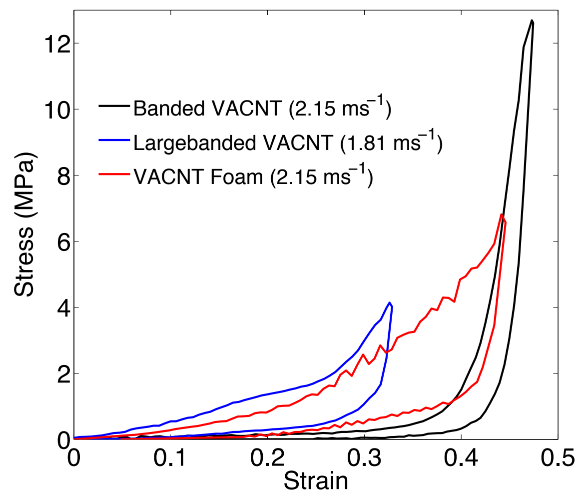

Figure 6.4. Comparison of the dynamic stress-strain responses of VACNT foams: (i) with a soft band synthesized for 2 min (banded VACNT), (ii) a soft band synthesized for 6 min (large-banded VACNT) and (iii) with no heterogeneous bands (continuous VACNT foams).

We used high-speed microscopy to visualize the deformation mechanisms *in-situ*, during dynamic compression of the samples. Snapshots from the high-speed microscopy and the corresponding stress-strain response for VACNT foam with a soft middle band, impacted at 0.85 m s^{-1} velocity are shown in the Figure 6.5. It should be noted that the sample appears inverted in the images, i.e. the section grown after the growth of soft middle band, which is found adjacent to the substrate in the as-grown sample is attached to the striker. The soft middle band appears darker than the other two sections as indicated on image (1) of Figure 6.5.

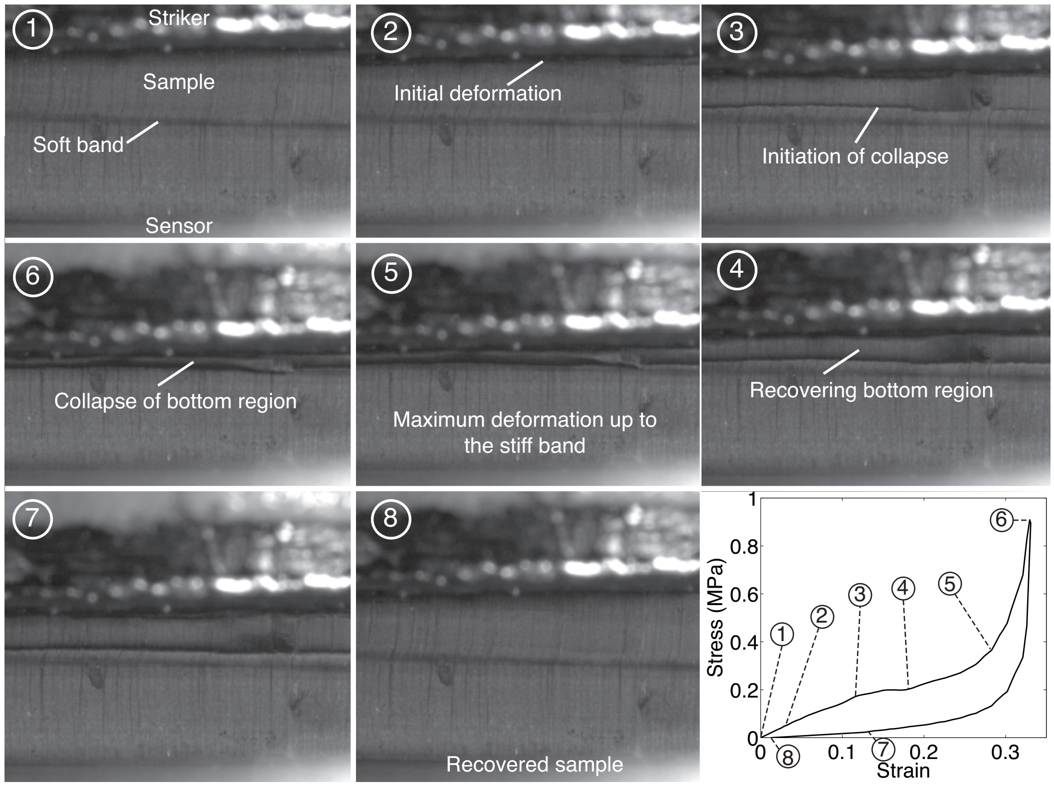

Figure 6.5. Snapshots from the high-speed microscopy showing the deformation mechanisms found in the dynamic compression of the VACNT foams with a middle soft band. The stress states corresponding to the deformations shown in the images are indicated as (1-8) on the dynamic stress-strain diagram. The sample was impacted at 0.85 m s^{-1} impact velocity.

When the sample is impacted, the deformation localizes first at the section adjacent to the striker, which is the weakest section of the sample as the final CNT growth occurs at the substrate interface during the termination of synthesis (image 2 of Figure 6.5.). The deformation progresses, compressing that section of the sample as the stress rises linearly. Following the linear regime, the stress progresses into a plateau regime as global buckling of the section occurs as indicated on image 3 of Figure 6.5. Until this instance, we do not notice any strain localization in the soft middle band. Stress rises moderately until both the bottom whole section and the soft middle band are compressed all the way up to the stiffest band and then rapidly increases as those two sections are densified. After reaching the peak stress, the striker unloads as the sample recovers. The stress rapidly decreases during the initial unloading and then slowly reaches zero as the sample recovers more than 95% of its deformation at the end of unloading. The recovery of all the samples tested in velocities between 0.5 and 7 m s^{-1} is 93.7±4.2 % on average. When samples are impacted at very high velocities, the stiffest band starts deforming with characteristic progressive buckling once the other two soft bands are completely deformed and densified.

We found that these deformation mechanisms in dynamic compression are very different from those of the quasistatic compression, found in the present study and in a previous study [193]. In the previous study, Raney et al., have shown that the intermediate soft bands collapse predominantly when a VACNT foam with multiple heterogeneous bands is compressed in a vice quasistatically (Figure 2 of [193]). When we performed *in-situ* high-speed microscopy along with a quasistatic compression test, we observed that the strain localizes first at the bottom region that was grown before the termination of the synthesis (the region of the sample that was adjacent to the substrate), similar to the dynamic case. This localized deformation progressed for a few more buckles and then localization occurred in the middle soft band, instead of progressing in the initial direction. During these deformations, stress rises almost linearly with strain. Subsequently, the bottom band undergoes a buckling as a whole during which the stress deviates from the linear trend and shows nonlinear rise in strain. The sample is compressed up to 50% strain in this experiment during which the stiffest band didn't show any observable deformation. During unloading, the sample recovers 73% of its strain, which is, although a significant recovery, much less compared to the recovery during dynamic compression.

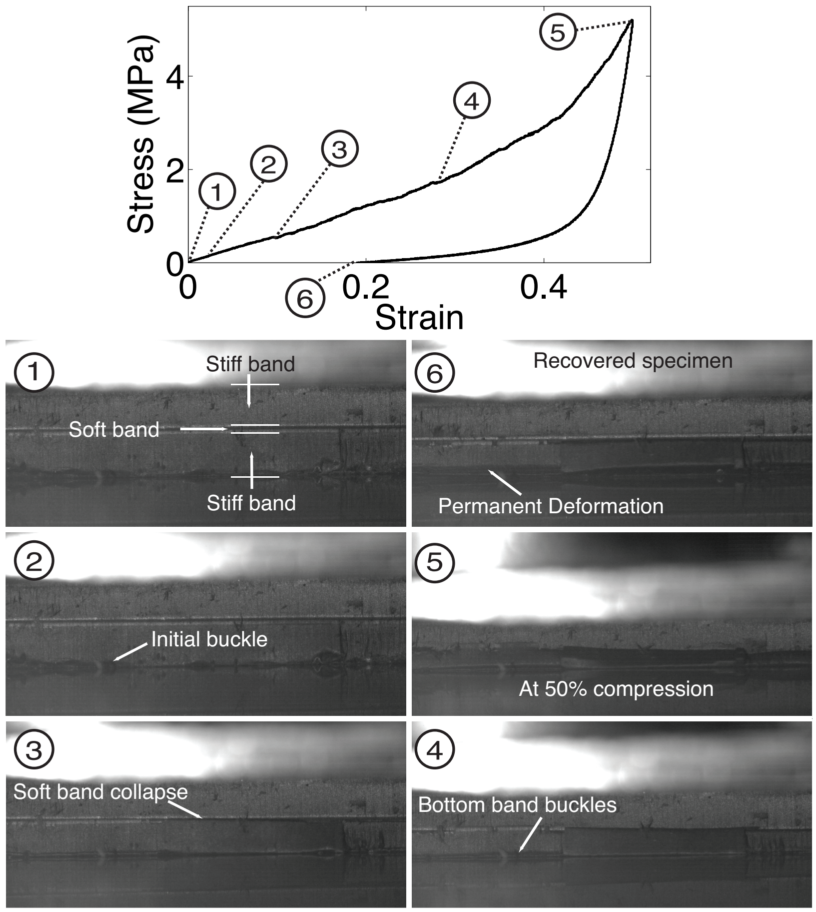

Figure 6.6. The stress-strain response and deformation mechanisms during quasistatic compression of a VACNT foam with heterogeneous bands (1-soft middle band). The stress-states corresponding to the snapshots from the high-speed microscopy are indicated as (1-6).

6.4 Conclusions

In summary, we performed impact experiments on the VACNT foams with heterogeneous bands to understand the fundamental role of the microscale heterogeneities on the bulk dynamic response and the deformation mechanisms. We found that the VACNT foams with heterogeneous bands exhibit a stress-strain response with well-defined linear, plateau and densification regimes when impacted at low-velocities (<2 m s^{-1}). When impacted at higher velocities, the samples deform at very low stress levels up to the complete deformation and densification of the bottom and middle soft bands and then show rapid increase with small strains as the stiffest-band starts deforming. We also showed that the deformation mechanisms in dynamics are significantly different from the deformation mechanisms found in the quasistatic compression. During dynamic compression, the deformation always localized at the bottom region (that was adjacent to the substrate during the termination of growth) of the sample and progressed towards the soft middle band. The soft middle band acts like a deformation-arrest barrier that prohibits further progression of the deformation, unless impacted at very high impact velocities. In contrast, during quasistatic compression, the strain localized in the weakest sections and slowly progressed to compress the rest of the samples. We also showed that the stress-strain response could be significantly tailored when the thickness of the soft middle band is increased. Our studies show that the microstructure of the VACNT foams can be engineered to achieve certain desirable deformation mechanisms and to tailor the stress-strain response in ways that are suitable for different protective applications.