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Auxetic materials with large negative Poisson's ratios based on highly oriented carbon nanotube structures

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Auxetic materials with large negative Poisson's ratios are fabricated by highly oriented carbon nanotube structures. The Poisson's ratio can be obtained down to −0.50. Furthermore, negative Poisson's ratios can be maintained in the carbon nanotube/polymer composites when the nanotubes are embedded, while the composites show much better mechanical properties including larger strain-to-failure (∼22%) compared to the pristine nanotube thin film (∼3%). A theoretical model is developed to predict the Poisson's ratios. It indicates that the large negative Poisson's ratios are caused by the realignment of curved nanotubes during stretching and the theoretical predictions agree well with the experimental results.
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Auxetic materials are materials with negative Poisson's ratios, which means that the lateral dimension expands during stretching.[1] They have long been investigated for their enhanced mechanical properties, for instance, shear modulus, break resistance, and superior toughness.[1–6] Auxetic materials have various applications, such as press-fit fasteners,[7] curved sandwich panels, flexible impact buffers,[8] soundproof materials,[9] and so on. In this report, we show that carbon nanotube (CNT) thin film with highly oriented structures exhibits obvious auxetic properties. The in-plane Poisson's ratio can be obtained down to −0.50, which is a large negative value, since most materials have positive Poisson's ratio commonly around 0.33. Furthermore, the negative Poisson's ratios can be maintained in the CNT/polymer composites when CNTs are embedded in the polymer matrix, while the composites show much better mechanical properties including larger strain-to-failure (up to ∼22%) compared to the pristine CNT thin film (∼3%), which are more applicable for practical applications. We also develop a model to predict the in-plane Poisson's ratios, and the theoretical predictions agree well with our experimental results. This study will encourage the study of the auxetic mechanism for related materials.

CNT paper (buckypaper), which is a paperlike CNT film, and their composites have become a hot topic in CNT research and have been widely investigated.[10–13] Recently, randomly oriented buckypapers have been found to have auxetic properties. The largest negative value of in-plane Poisson's ratio for the buckypapers fabricated by 100% multiwalled nanotubes was −0.20.[14,15] Since 2002, a method for synthesizing superaligned and ultrathin continuous CNT sheets has been developed.[16–18] These sheets have many useful applications, such as loudspeakers,[19] transmission electron microscopy grid[20] and so on. In this report, we used these superaligned sheets to construct CNT thin films with highly oriented structures, and examined their in-plane Poisson's ratio properties. First of all, one layer of continuous and aligned CNT sheet was directly drawn from superaligned CNT arrays by a solid state process and was put on a stainless steel frame. The 100 layer biaxial CNT film was obtained by repeating the drawing process, and stacking the CNT sheets in two perpendicular directions alternatively [Fig. 1(a), inset part]. These sheets were loosely stacked and it was difficult to detach the entire film from the frame perfectly. Then densified sheets were achieved by immersing the frame with the attached sheets in a liquid (such as ethanol). Surface tension effects during ethanol evaporation shrank the sheets with thickness down to ∼3 μm, and the densified CNT film can be easily released from the frame. The micro-

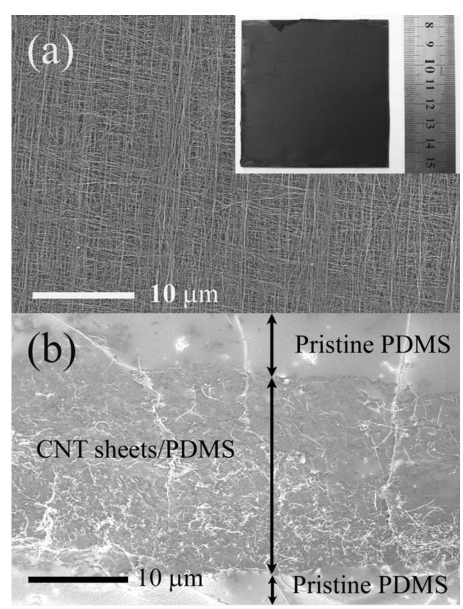

FIG. 1. CNT thin films and CNT/PDMS composite: (a) SEM image showing the surface of a CNT thin film containing 100 layers of CNT sheets aligned in two perpendicular directions. The inset part is a photograph of 100 layer CNT sheets stacking on a steel frame. (b) Cross sectional SEM image of a CNT sheets/PDMS composite.

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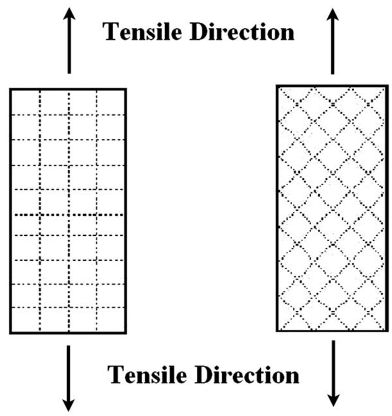

FIG. 2. Schematic illustrations of the samples: dashed lines represent the alignment of CNT sheets. Half of the CNT sheets' alignment was along the tensile direction, and the other half was perpendicular to the tensile direction (left panel). The alignment of the CNT sheets forms an angle of 45° with the tensile direction (right panel).

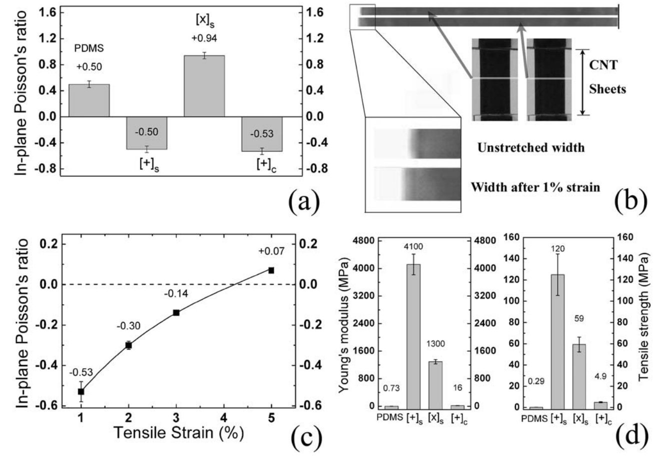

FIG. 3. Mechanical properties of CNT thin films and CNT/PDMS composites: (a) The in-plane Poisson's ratios of pristine PDMS, $[+]_s$, $[\times]_s$, and $[+]_c$ samples at a small strain (1%). (b) Photographs showing the width change in the sample before and after tensile test. (c) The changes of in-plane Poisson's ratios of $[+]_c$ samples with increasing strain. (d) Young's modulus and tensile strength of pristine PDMS, $[+]_s$, $[\times]_s$, and $[+]_c$ samples.

graphs of the densified sheets were probed by scanning electron microscopy (SEM) [Fig. 1(a)]. CNTs are continuous and highly oriented in the film forming a grid network.

We also fabricated CNT/polymer composites by infiltrating liquid polymer into a stack of continuous and aligned multiwalled CNT sheets and curing the polymer afterwards at room temperature.[21] The polymer matrix here is polydimethylsiloxane (PDMS), which is a transparent and flexible polymer and has a very large strain-to-failure (>150%). The weight fraction of CNTs in the composite was calculated to be 0.86 wt %.[22] The internal architecture of the CNT/PDMS composite was characterized by cross sectional SEM imaging [Fig. 1(b)].

All samples were made into strips with dimensions at $20\times 10\ \mathrm{mm}^2$ (length × width). They were cut in two ways (Fig. 2). In one way, half of the CNT sheets' alignment was along the tensile direction and the other half was perpendicular to the tensile direction (Fig. 2, left panel). The pristine CNT sheets tested in this way were labeled as $[+]_s$ (s is short for "sheet"). In the other way, the alignment of the CNT sheets forms an angle of 45° with the tensile direction (Fig. 2, right panel). The pristine CNT sheets tested in this way were labeled as $[\times]_s$.

The in-plane mechanical properties measurements were held at room temperature by using Instron 5838 Microtester. The crosshead speed was 0.005 mm/sec. A digital camera (Fuji 5800fd) was used to capture images for measurement of the changes of film width during tensile test. Then accurate in-plane Poisson's ratio was obtained from the captured images by using "ADOBE PHOTOSHOP 7.0.1" to compare the corresponding strains in transverse and tensile directions.

The in-plane Poisson's ratios of pristine PDMS, $[+]_s$ and $[\times]_s$ samples at a small strain (1%) are shown in Fig. 3(a). The Poisson's ratio of pristine PDMS is +0.50. The Poisson's ratio of pristine CNT film sample $[+]_s$ was down to −0.50, which is a negative value larger than that of the buckypaper in which CNTs are randomly oriented.[14] The width change in the sample before and after tensile test is shown in Fig. 3(b). However, the Poisson's ratio of $[\times]_s$ sample was up to +0.94, which is a positive value, exhibiting a diverse feature compared to the $[+]_s$ sample. Such a Poisson's ratio is a classical behavior of a 45° fiber cross ply. Therefore, this kind of CNT film material is highly anisotropic, allowing either large positive or negative Poisson's ratio to be obtained in one material, even if they were cut from the same preform before test. The only difference is the angle between CNT alignments in the sheets and the tensile direction.

Since we are more interested in the auxetic properties, the CNT/PDMS composite sample, in which the embedded CNT alignment is the same as $[+]_s$ sample, was also examined. It was labeled as $[+]_c$ (c is short for "composite"). The in-plane Poisson's ratio of $[+]_c$ sample is also shown in Fig. 3(a). The negative value was down to −0.53, which is close to that of the $[+]_s$ sample. Therefore, it is a kind of auxetic composite and negative Poisson's ratios can be maintained in the composite when the highly oriented CNT structures are embedded in the flexible elastomer. Since pristine PDMS has a positive Poisson's ratio, it must be the embedded CNT sheets that cause the auxetic property.

The flexible auxetic composites have many advantages, including larger strain-to-failure, flexibility and protection function. The $[+]_s$ sample has a strain-to-failure of ~3%, while the value of $[+]_c$ sample increases up to ~22%. It will be more applicable for practical applications where large strains are needed. When CNT sheets are directly exposed to external environment, they are fragile and easily stick to other surfaced due to van der Waals force. When CNTs are embedded into PDMS, they will not be exposed to external environment directly, while the auxetic property can still be maintained in the composite. The PDMS serves as a protection layer here.

Furthermore, we observed that the Poisson's ratios for the $[+]_c$ sample varied from −0.53 to +0.07 as tensile strain increased from 1% to 5% [Fig. 3(c)]. This phenomenon can be easily understood and explained as follows. It is the van der Waals force that makes the CNTs join end to end, forming continuous and aligned CNT sample $[+]_s$. With increasing strain, CNTs in the composite will be broken at the ends and their influences on the changes of sheet width are weakened. Figure S1 shows that complete unloading did not return the sample to its original length, which shows some irreversibility.[22]

Young's modulus and tensile strength were also measured [Fig. 3(d)]. The pristine CNT films show a much higher Young's modulus and tensile strength compared to the composites. The Young' modulus of the composites $[+]_c$ is 16 MPa. It is much smaller than that of the pristine CNT films, which is 4100 MPa. The effect of PDMS content on tensile strength follows the same trend with Young's modulus.

We developed a model to predict the in-plane Poisson's ratios.[22] In the model, CNTs form a grid network on the x-y plane. Actually, sheet layers are not strictly parallel to each other due to the curves of CNTs. The complex morphology of the curved CNTs in the thickness direction is depicted as a zigzag set of struts for simplicity (Fig. S2).[22] There are two kinds of deformation, corresponding to the $[+]_s$ sample [Fig. S3(a)] and the $[\times]_s$ sample [Fig. S3(b)], respectively.[22] The following elastic deformations were taken into consideration: the effective force constant k_{sb} of a single zigzag CNT combining both strut stretch and angle deformation, and changes in the torsional angle Φ, expressed by the torsional force constant k_t. The ratio of the effective force constant k_{sb} to the torsional force constant k_t is R.[15,22]

For the $[+]_s$ sample, the connectivity of the zigzag forces the nanotubes to expand in all directions like an umbrella; hence producing a negative Poisson's ratio in the plane of the structure [Fig. S3(d)].[22] Therefore, the realignment of curved CNTs results in the negative in-plane Poisson's ratio. The total energy needed for a given small tensile strain in terms of strut length changes and angle changes can be obtained. Then minimization of the energy provides all changes in lengths and angles for a specified small tensile strain in the in-plane direction. The in-plane Poisson's ratios is given by $\nu_1=-(R+1)/(2R+1)$ (for the case $R<1$) or $\nu_1=-(R-1)/(2R+1)$ (for the case $R>1$). Following a similar deduction process, the in-plane Poisson's ratio of the $[\times]_s$ sample can be obtained as $\nu_1'=(R-2)/(R+2)$.[22] It can be seen that when changes in nanotube length are negligible compared to the changes in angles, expressed as $R\rightarrow\infty$, the Poisson's ratios $\nu_1\rightarrow-0.5$ and $\nu_1'\rightarrow 1$ are obtained.

The assumption of $R\rightarrow\infty$ is quite reasonable, because the Young's modulus of the continuous and aligned CNT sheets is very high along the CNT sheets' alignment direction [Fig. 3(d)]. It means that CNTs are so "rigid" that it is difficult to change the nanotube length, even if the curves of nanotubes were taken into consideration. Hence, the effective force constant k_{sb} is much larger than torsional force constant k_t, resulting in $R\rightarrow\infty$. The predicted Poisson's ratios ($\nu_1\rightarrow-0.5$, $\nu_1'\rightarrow 1$) is consistent with our experiment results, in which $[+]_s$ sample has a negative Poisson's ratio of −0.50 and $[\times]_s$ sample has a positive Poisson's ratio of +0.94.

In summary, we have demonstrated an auxetic material based on highly oriented CNT structures. Auxetic composites based on this structure have also been fabricated, which have a number of advantages in terms of larger strain-to-failure, flexibility, and protection function. The CNT/PDMS composites show large negative in-plane Poisson's ratios at low strains. Furthermore, a model was developed to predict the Poisson's ratios, and the theoretical predictions agree well with our experimental results. This study points out a direction for fabricating auxetic materials with high performance and provides valuable information for the design of artificial muscles, gaskets, strain sensors, and so on.

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[1] R. S. Lakes, Science **235**, 1038 (1987).
[2] K. E. Evans, M. A. Nkansah, I. J. Hutchinson, and S. C. Rogers, Nature (London) **353**, 124 (1991).
[3] K. L. Alderson and K. E. Evans, Polymer **33**, 4435 (1992).
[4] R. S. Lakes, Adv. Mater. (Weinheim, Ger.) **5**, 293 (1993).
[5] R. H. Baughman, Nature (London) **425**, 667 (2003).
[6] X. Tan, W. Jo, T. Granzow, J. Frederick, E. Aulbach, and J. Rödel, Appl. Phys. Lett. **94**, 042909 (2009).
[7] J. B. Choi and R. S. Lakes, Cell. Polym. **10**, 205 (1991).
[8] R. S. Lakes, J. Mech. Des. **115**, 696 (1993).
[9] C. P. Chen and R. S. Lakes, Cell. Polym. **8**, 343 (1989).
[10] J. Liu, A. G. Rinzler, H. J. Dai, J. H. Hafner, R. K. Bradley, P. J. Boul, A. Lu, T. Iverson, K. Shelimov, C. B. Huffman, F. Rodriguez-Macias, Y. S. Shon, T. R. Lee, D. T. Colbert, and R. E. Smalley, Science **280**, 1253 (1998).
[11] S. M. Cooper, H. F. Chuang, M. Cinke, B. A. Cruden, and M. Meyyappan, Nano Lett. **3**, 189 (2003).
[12] M. Endo, H. Muramatsu, T. Hayashi, Y. A. Kim, M. Terrones, and N. S. Dresselhaus, Nature (London) **433**, 476 (2005).
[13] D. Wang, P. C. Song, C. H. Liu, W. Wu, and S. S. Fan, Nanotechnology **19**, 075609 (2008).
[14] L. J. Hall, V. R. Coluci, D. S. Galvão, M. E. Kozlov, M. Zhang, S. O. Dantas, and R. H. Baughman, Science **320**, 504 (2008).
[15] V. R. Coluci, L. J. Hall, M. E. Kozlov, M. Zhang, S. O. Dantas, D. S. Galvão, and R. H. Baughman, Phys. Rev. B **78**, 115408 (2008).
[16] K. L. Jiang, Q. Q. Li, and S. S. Fan, Nature (London) **419**, 801 (2002).
[17] X. B. Zhang, K. L. Jiang, C. Teng, P. Liu, L. Zhang, J. Kong, T. H. Zhang, Q. Q. Li, and S. S. Fan, Adv. Mater. (Weinheim, Ger.) **18**, 1505 (2006).
[18] K. Liu, Y. H. Sun, L. Chen, C. Feng, X. F. Feng, K. L. Jiang, Y. G. Zhao, and S. S. Fan, Nano Lett. **8**, 700 (2008).
[19] L. Xiao, Z. Chen, C. Feng, L. Liu, Z. Q. Bai, Y. Wang, L. Qian, Y. Y. Zhang, Q. Q. Li, K. L. Jiang, and S. S. Fan, Nano Lett. **8**, 4539 (2008).
[20] L. Zhang, C. Feng, Z. Chen, L. Liu, K. L. Jiang, Q. Q. Li, and S. S. Fan, Nano Lett. **8**, 2564 (2008).
[21] Q. F. Cheng, J. P. Wang, K. L. Jiang, Q. Q. Li, and S. S. Fan, J. Mater. Res. **23**, 2975 (2008).
[22] See EPAPS supplementary material at http://dx.doi.org/10.1063/1.3159467 for experimental details and theoretical calculation of in-plane Poisson's ratio for carbon nanotube sheets.