Light induced reversible and irreversible mechanical responses in nanotube-polymer composites

CrossMark

Xudong Liang [a, 1], Zichen Zhang [b, 1], Abhishek Sathisha [a, 1], Shengqiang Cai [a, c], Prabhakar R. Bandaru [a, c, *]

[a] Department of Mechanical and Aerospace Engineering, University of California, San Diego, La Jolla, CA 92093, USA
[b] Department of NanoEngineering, University of California, San Diego, La Jolla, CA 92093, USA
[c] Material Science Program, Department of Mechanical and Aerospace Engineering, University of California, San Diego, La Jolla, CA 92093, USA

ARTICLE INFO

ABSTRACT

It is shown that visible light irradiation of carbon nanotube (CNT) dispersed polymers may yield both reversible and irreversible changes in measured mechanical stress. While light irradiation of PDMS (polydimethylsiloxane)−CNT composite yields a change of stress level at a fixed strain, which reverts to the original value after the incident light is removed, the RET (reactive ethylene terpolymer)−CNT composite exhibits such reversible characteristics as well as an additional irreversible stress-relaxation response when the composite is first irradiated by light. A microscopic model is proposed to explain the mechanism of the dual photomechanical responses of the RET-CNT composites and quantitative predictions are compared with experimental measurements.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Photo-responsive (PR) materials have been extensively explored for various engineering applications, from the nano-to the macro-scale [1,2], *e.g.*, in photo-switchable ion transport [3], photon-propelled robotics [4] and photo-responsive actuators [1,4]. In comparison to other actuation mechanisms, PR material constituted devices have the advantages of not requiring physical contact to a powering source, which enable structure compactness and related weight reduction [2]. Moreover, various light irradiation parameters (intensity, frequency, polarization, etc.) [4,5], can be used for external control.

PR material has been synthesized mostly through assembling specific molecules into host materials [6−8], where upon light irradiation, configurational change related to such molecules can cause macroscopic mechanical responses [9]. For example, azobenzene molecules incorporated in photo-responsive composite yield a mechanical response due to a reversible *cis*-trans transformation driven by light irradiation [10−12]. To maximize the photo-response in PR materials, polymer composed of photoactive units [13,14], such as covalently linked photoisomerizable azobenzene moieties [15] incorporated into copolymers [16,17]. Recent studies have found that composites formed through dispersing carbon nanotubes (CNTs) [4,18−20], boron nitride [19] or molybdenum disulfide [21] into polymer matrices may also behave as PR materials. Various light-induced deformation modes including bending [22], contraction [23] and expansion [5] have been shown in CNT-infiltrated polymeric composites. Such responses have been considered inherent to the composite, and were not observed in either the native polymer or CNTs [24,25]. For instance, it has been reported that multiwalled carbon nanotube (MWCNT) dispersed polydimethylsiloxane (PDMS) composites [26] can expand at small pre-strain while contracting at large pre-strain when exposed to light irradiation with wavelength ~ 675 *nm* [18,27]. Such effects have been attributed to stretch-induced alignment of embedded CNTs and the kink-instability upon photon absorption [18].

In this paper, we study the photo-response of the MWCNT dispersed reactive ethylene terpolymer (RET) composites. RET is a commercially available thermoplastic elastomer, which has good adhesive properties to metals and is widely adopted as coatings that protect metal structure from corrosive environments and mitigate cathodic disbondments [28,29]. The elastomeric characteristics and corrosion resistance are also critical to the utility of

* Corresponding author. Department of Mechanical and Aerospace Engineering, University of California, San Diego, La Jolla, CA 92093, USA.
*E-mail address:* pbandaru@ucsd.edu (P.R. Bandaru).
[1] These authors contribute equally.

RET as a hot-melt adhesive and coating [30] and the constituent epoxide group enables effective anchoring with functional groups(*e.g.*, -OH, -COOH, -NH$_2$ etc.) on the CNTs [31,32].

In the stretched RET-MWCNT composite, in addition to photo-mechanical stress modulation similar to that previously observed in PDMS-MWCNT composites [18,27,33], an irreversible and significant stress relaxation was observed under initial light irradiation. We propose a microscopic model to explain such phenomena, by invoking the transformation of crystalline to amorphous domains due to light irradiation. Our results and analyses would be useful for a better understanding of PR composites and pave the way for their application.

2. Experiments

The studied composite was synthesized from a RET polymeric matrix with dispersed MWCNTs. The embedded MWCNTs (obtained from Sigma-Aldrich Inc.) have an average diameter of 140 *nm*, with the length ranging from 5 to 9 *μm* and density 2.1 *g/cm³*. RET (DuPont™, Elvaloy® 4170, density 0.94 *g/cm³*) is constituted from epoxide, butyl and ethylene groups (Fig. 1a). The epoxide group has a high reactivity [30] and is amenable [34] for effective anchoring of constituent ring bonds with functional groups on the CNTs [35,36]. The butyl groups (*soft segments*) provide high extensibility in the polymer at ambient temperature; while the ethylene groups (*hard segments*) induce formation of crystalline domains [37,38], and serve as the physical cross-linking [39] in the RET matrix. Such molecular structure characteristics make RET behave like an elastomer at room temperature and as a polymer melt at higher temperature. Therefore, RET may be regarded as thermoplastic elastomer (TPE) [9,40].
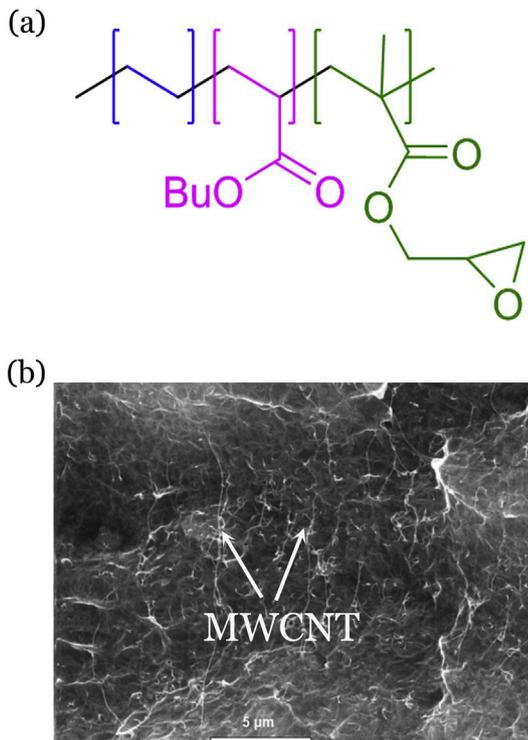

Fig. 1. (a) Chemical structure of the RET (Elvaloy® 4170) with three functional groups: the ethylene group (blue), the butyl group (purple) and the epoxide group (green). (b) Scanning electron microscopy (SEM) image of the RET-MWCNT composite. The sample is for a 7 wt% MWCNT composite, with initially non-aligned MWCNTs distributed among the RET matrix. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

To prepare the composites, pellets of RET were first dissolved in toluene which was heated to ~60 °C for 2 h. The CNTs were also dispersed in toluene by using a sonicator (VCX-750, Sonic Materials Inc., 750 *W*, 42 *kHz*) for 10 min. The CNT-toluene dispersion was then incorporated with the RET solution and sonicated again for 1 h. The mixture was stirred for another 2 h before being placed in a vacuum oven (under pressure at 0.866 atm) at 60 °C for 10 h. A scanning electron microscopy (SEM) image of a RET-MWCNT composite is shown in Fig. 1b, indicating non-aligned MWCNTs distributed among the RET matrix. In this paper we report on a representative 7 wt% CNT constituted RET composite. Such a weight fraction was above the percolation threshold of CNTs (of ~2.3 wt% for the given MWCNT length and diameter) [35,41] and consequently MWCNTs form a connected network in the polymer matrix [42].

Stress-strain diagrams of RET composite were measured (5965 Dual Column Testing systems, Instron). The RET-MWCNT composite was cut into samples of dimensions, 25 *mm* × 5 *mm* × 0.3 *mm*. The samples were firmly clamped by the grippers and subjected to a uniaxial tensile stress. The accuracy of the strain measured in the sample was within ±0.1%. While the composites were stretched, they were exposed to irradiation (of area ~100 *mm²*) from a light source (CREE XM-L2 LED, maximum intensity at ~ 440 *nm*, 10 mW/cm² at 1 *m* distance) positioned at a distance of 0.15 ± 0.01 *m* away from the surface of the sample, and the light intensity (measured by Spectra-Physics 407A) was modulated through neutral density filters (Thor Labs Inc.) in the range of 0–97 mW/cm². The latter limit of irradiance is close to the standard of solar irradiance (~"1 sun") of ~100 mW/cm².

3. Results and discussion

Fig. 2 indicates the photomechanical response characteristics of stretched RET-MWCNT composite under light irradiation. The composite was first stretched and held at a constant strain: 50% ($\varepsilon = 0.5$) for 1000 s, to enable a quasi-equilibrium state of the sample before light irradiation. Subsequently, two periods of light irradiation (marked in yellow in Fig. 2) were provided under a
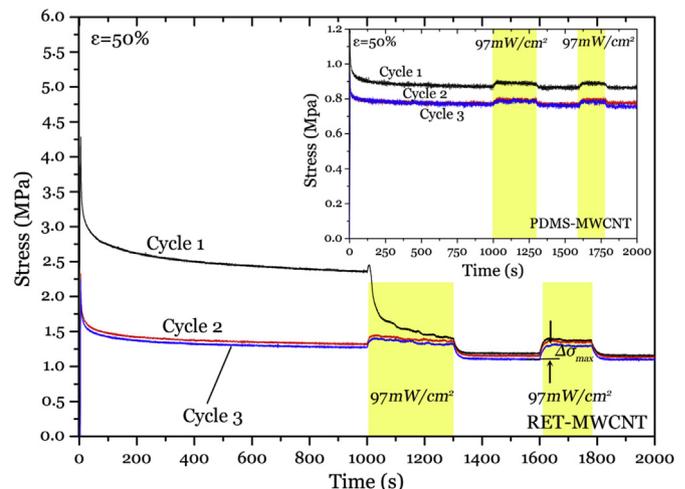
Fig. 2. A single RET-MWCNT composite (7 wt%) under a 50% pre-strain and light irradiation of intensity 97 mW/cm². Three cycles of test were performed, each included a mechanical equilibration step, two periods of light irradiation and a stage after removing external constraints. The RET-MWCNT composite showed a dramatic decrease in stress under the first light irradiation period in Cycle 1, with repeatable stress modulations for the subsequent light irradiations. The inset indicates the stress response in PDMS-MWCNT composite (7 wt%) under the same test procedures, showing only repeatable stress modulations for all light irradiation periods. The maximum stress responses under light irradiation were measured as Δσmax.

constant intensity of 97 mW/cm². After switching off the second light irradiation, the mechanical constraint was removed at 2000 s and the composite contracted in a stress free state for another 900 s. The aforementioned steps define a cycle of the photo-response in our testing. Three nominally identical cycles (Cycle 1, 2 and 3 in Fig. 2) of tests were conducted on a single sample by stretching to the same length. After Cycle 1, considerable plastic deformation was introduced in the sample. We measured the stress as a function of time in each cycle, and observed distinct responses upon light irradiations. In Cycle 1, after a small increase of stress, a significant stress relaxation was observed when the sample was exposed to light for the first time. The stress decreased further when light was removed at the end of the first irradiation. In the second period of irradiation in Cycle 1 as well as those in Cycles 2 and 3, a different stress response was detected. The stress increased as the light being switched on, remained at a constant value during the light irradiation, and returned to the original value when light was turned off. Such a repeatable stress modulation was also observed in the PDMS-MWCNT composite (7 wt%) tested under the same procedures as the RET-MWCNT composite. The results are shown in the inset of Fig. 2, showing only repeatable stress modulations for all light irradiation periods.

The significant stress relaxation in the RET-MWCNT composite, which was only observed during the first light irradiation in Cycle 1, and not detected in the PDMS-MWCNT composite, will be referred to as an 'irreversible' response. Alternately, the subsequent stress modulations upon light irradiation are similar in RET-MWCNT as well as PDMS-MWCNT composites, and constitute a 'reversible' response. The latter aspect has been previously reported in PDMS-MWCNT composite [1,18,25,33], and was postulated as due to buckling of constituent CNTs caused by the surrounding aligned polymer chains [18,25]. In order to quantitatively compare two types of photo-response observed in the RET-MWCNT composite, the stress response ($\Delta\sigma$) over the light irradiation time (t) under a constant strain was modeled through the relation [25],

$$\Delta\sigma = \Delta\sigma_{max}\left(1 - \exp\left(-(t/\tau)^{\beta}\right)\right), \tag{1}$$

where $\Delta\sigma_{max}$ is the maximum magnitude of stress response as shown in Fig. 2, t is the time which is shifted to model the photo-response initiation at $t=0$ s, and τ is a relaxation time constant. Following Equation (1), for reversible response in RET-MWCNT composite, the fitting parameters indicated a $\tau \approx 12$ s and $\beta = 2$ (as detailed in *Supplementary Information:* Fig. S1a), similar to the photo-response reported in PDMS-MWCNT composite [25]. For the irreversible stress relaxation, a similar exponential function was adopted [25]. By assuming the stress response under first irradiation to be a mixture of irreversible and reversible response, we obtained the irreversible response by subtracting the stress modulation under the second irradiation. The fitting revealed a relaxation time $\tau \approx 19$ s and $\beta = 1$ (Fig. S1b), indicating the exponential relaxation kinetics commonly observed in polymeric materials [43]. The different values of β ($\beta = 1$ for the irreversible response and $\beta = 2$ for the reversible response) clearly indicated two distinct photo-response mechanisms under the first and the subsequent irradiation. Additionally, the RET-MWCNT composite took about 8 s to initiate the relaxation in the irreversible response; while the reversible response started much faster (<1 s) as shown in Fig. S1. The difference in the response time may have arisen from the different amount of thermal energy required, in accordance with the earlier proposed model [18].

The distinct photo-response between the PDMS and RET composites with identical weight percentage of MWCNTs (7 wt%) indicate that the nature of polymer matrix should be essential to

the phenomena shown in Fig. 2. Different from the covalently crosslinked PDMS, RET is a thermoplastic elastomer [40], where the ethylene segments form crystalline domains that serve as physical crosslinks [35]. Upon temperature changes, such a crystalline structure can be reversibly melted and recrystallized [37,38]. We propose that the dispersed CNTs absorb incident light irradiation and convert it to thermal energy [23], consequently melting the crystalline domains, given that the melting temperature of RET is known to range between 29.9 and 87 °C [36]. The transformation of crystalline domains to amorphous domains in the RET matrix is hypothesized to be responsible for the observed irreversible response.

To examine the proposed hypothesis and mechanisms, we conducted tests of the RET-MWCNT composite subjected to mechanical stretch and light irradiation simultaneously to reveal the change of number density of crystalline domains. The strain rate for the test was set to be $10^{-4}/s$, to ensure that the sample is close to an equilibrium state during the stretch. In the uniaxial tension test, the stress can be related to stretch through a neo-Hookean model, commonly adopted for elastomeric materials [44],
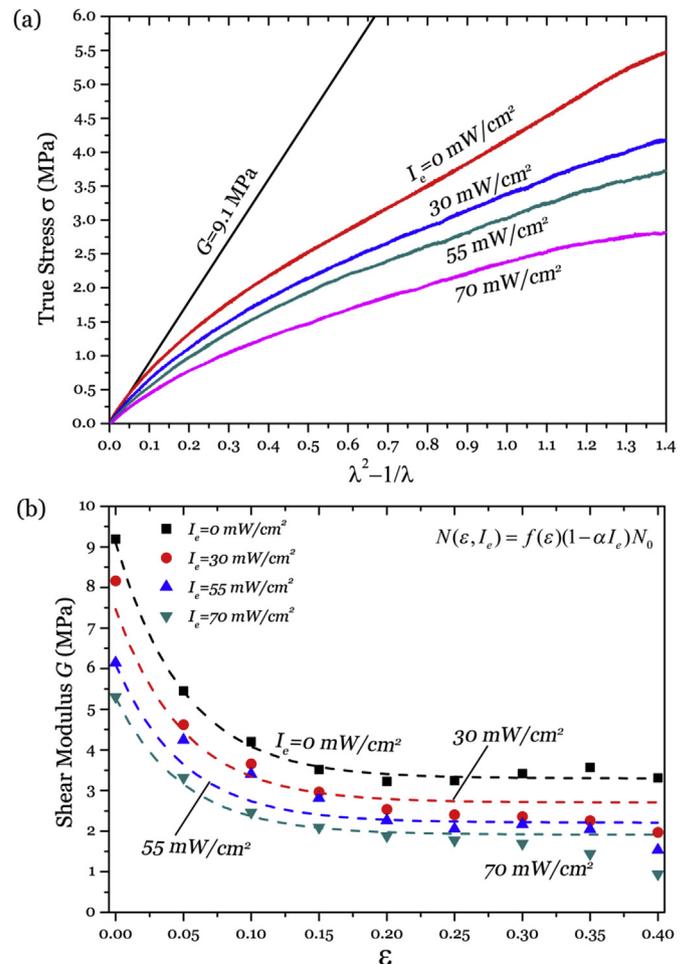
Fig. 3. (a) Stress and stretch relation of RET-MCNT composite in uniaxial tensile test with strain rate at $10^{-4}/s$. In addition to the results from different light intensities, the relation for a neo-Hookean material ($G = 9.1$ MPa) was plotted. (b) The shear modulus G under different light intensities (in dots) with respect to strain ε. The fitting results were shown as dashed lines. By assuming number of crystalline domains changed linearly with light irradiation intensity ($G = Nk_BT$), the measurements was fit the expression: $N(\varepsilon,E_e) = (f(\varepsilon)(1-\alpha I_e))N_0$. N_0 is the number density of the crystalline domains without pre-strains and light irradiation. $f(\varepsilon)$ is a dimensionless exponential function of strain ε. α is the fitting parameter related to light irradiation, with $\alpha = 0.006$ cm²/mW. The fitting results were shown as dashed lines.
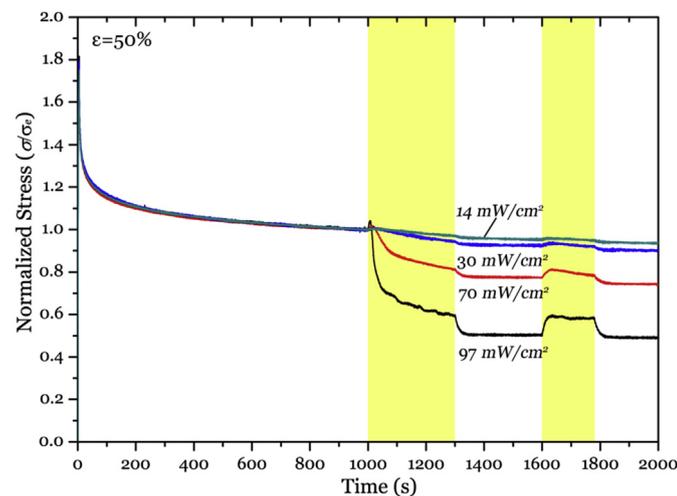
$$\sigma = G\left(\lambda^2 - 1/\lambda\right), \tag{2}$$

where σ is the true stress, λ is the stretch ($= 1+\varepsilon$) and defined as the ratio of the deformed length to initial length of the sample and G is the shear modulus of the material, which is linearly proportional to the number density of the crystalline domains (N) [39,44], and expressed as $G = Nk_BT$ [44], where k_B is the Boltzmann constant and T is the temperature. As shown in Fig. 3a, the measured relationship between true stress and ($\lambda^2 - 1/\lambda$) was nonlinear. The stress was smaller than the value given by neo-Hookean model in the absence of light irradiation ($I_e = 0$), which is similar to the softening effect due to the breakdown of attachment under stretch in rubber-filler composites [45−47]. Such softening observed in RET-MWCNT composite was further enhanced under light irradiation with increasing intensity. To obtain the change of the shear modulus of the RET composite under light irradiation, we calculated the slope of curves in Fig. 3a as a function of strain and plotted the results in Fig. 3b. It was found that the G of the composite decreased with the increase of the strain (ε), with a greater drop under a larger light intensity (I_e). The light irradiation induced reduction in the shear modulus supports our hypothesis related to the melting of the crystalline structure.

Based on the experimental measurements, we estimate the number density of the crystalline domains [39,44]: $N(\varepsilon, I_e)$, with respect to the strain ε and light intensity I_e through:

$$N(\varepsilon, I_e) = N_0 f(\varepsilon)(1 - \alpha I_e), \tag{3}$$

where N_0 is the number density of the crystalline domains without pre-strain and light irradiation. $f(\varepsilon)$ represents the softening effect induced by mechanical stretch at $I_e = 0$, and was fitted to a phenomenological expression of the exponential form [45,48]: $f(\varepsilon) = 0.34 + 0.66\exp(-\varepsilon/0.05)$. The reduction of $N(\varepsilon, I_e)$ was assumed to be linearly dependent on I_e, and can be represented by a dimensionless function: $(1 - \alpha I_e)N_0$, where $\alpha = 0.006\ cm^2/mW$ is a fitting parameter for light intensity ranging from 0 to 70 mW/cm^2. The fitting results are plotted as dash lines in Fig. 3b, which agree well with the experimental observations.

To further probe the relation between the photomechanical response and the light intensity, the stress response of the RET-MWCNT composites were measured under a fixed pre-strain and light irradiation with intensities ranging from 14 to 97 mW/cm^2. Similar to the setup related to Fig. 2, two periods of light irradiation were applied to the composites, after applying strain (50%) for 1000 s to ensure mechanical equilibrium state. The stress responses for different light intensities were normalized by the equilibrium stresses (σ_e) recorded before light irradiation and are compared in Fig. 4. The magnitude of the stress response in the RET-MWCNT composite increased with light intensity, indicating a greater reduction of $N(\varepsilon, I_e)$ in the RET matrix. Indeed, detailed measurements with successive decrease or increase of the light intensity in a single RET-MWCNT composite further validates our hypothesis related to light irradiation induced melting of crystalline domains (as indicated in *Supplementary Information:* Fig. S2). As shown in Fig. S2a, we observed that when light intensity was gradually reduced from 97 to 14 mW/cm^2 in a RET-MWCNT composite with a 30% pre-strain, the stress (proportional to $N(\varepsilon, I_e)$) reached minimum after the first light irradiation step. The subsequent light irradiations with lower intensity do not seem to be able to change $N(\varepsilon, I_e)$, which leads to photomechanical stress response similar to Cycle 1 of Fig. 2. Alternately, through gradually *increasing* the light
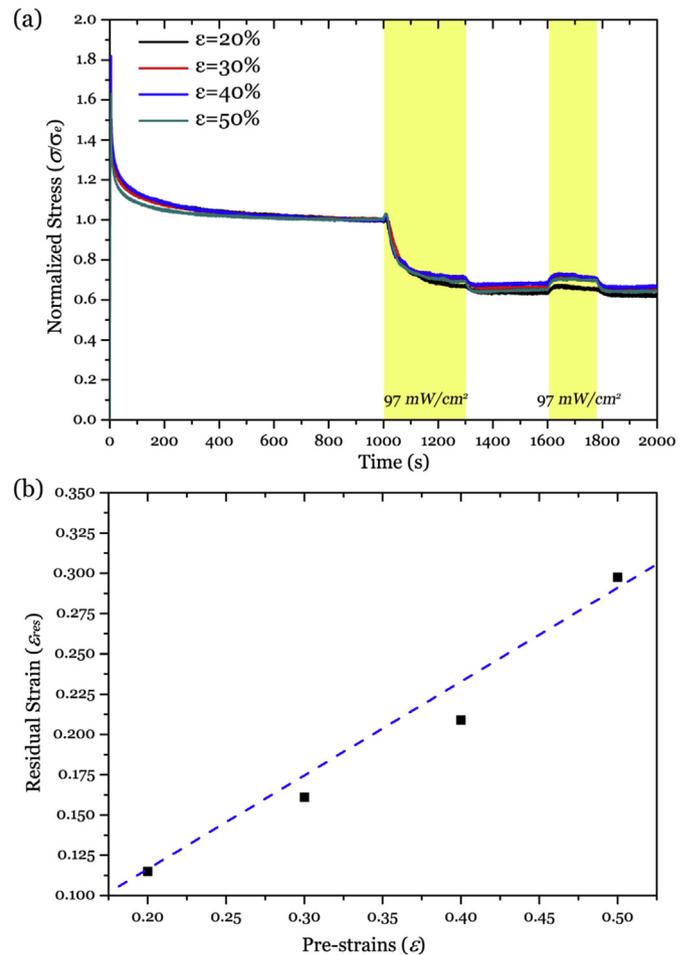
Fig. 5. (a) Photo-response under different pre-strains (20%, 30%, 40% and 50%) with light irradiation intensity of 97 mW/cm^2. After normalized to the equilibrium stress (σ_e) recorded before light irradiation, the stress responses under different pre-strains collapsed to a single curve. (b) Relation between the residual strains (ε_{res}) and the applied pre-strains (ε) in a freestanding RET-MWCNT composite after light irradiation in stretched state. The experimental measured residual strains were plotted in dots, while the dashed line was the prediction of residual strain based on the microscopic model shown in Fig. 6.

Fig. 4. Photo-response under different light irradiation intensities, ranging from 14 to 97 mW/cm^2. Two periods of light irradiation were applied to the composites after stretched to a 50% pre-strain. The stress responses under different light intensities were normalized to the equilibrium stress (σ_e) recorded before light irradiation, showing a growing magnitude in stress relaxation with an increase of light intensity under the first light irradiation.

intensity from 14 to 97 mW/cm^2, $N(\varepsilon, I_e)$ was diminished after each light irradiation step, and multiple *irreversible* stress relaxations were detected (Fig. S2b). In summary, by controlling $N(\varepsilon, I_e)$, we would be able to tune the material properties as well as the photomechanical response in RET-MWCNT composites.

We further studied the role of pre-strain in modulating the photo-response in RET-MWCNT composites. By varying the pre-strains ranging from 20% to 50%, the composites were subjected to two periods of light irradiation with constant intensity of 97 mW/cm^2. The variation of stress under different pre-strains were normalized to the correspondent σ_e recorded before light irradiation. It is shown in Fig. 5 that all of the normalized stress responses under different pre-strains collapse to a single curve

during first light irradiation period, indicating that the effect of stretching of the polymer chains was not coupled with the light irradiation for the irreversible response. Alternately, the reversible stress response under the second period of light irradiation showed a tunable modulation with respect to pre-strains, similar to previous observations in PDMS-nanotube composites [5,18]. On this basis, we can conclude that the reason for the irreversible stress relaxation is the melting of crystalline domains in the RET matrix, facilitated by the light-to-thermal energy transduction in CNTs. The alignment of CNTs under different pre-strains, which was believed to be related to the stress modulation in PDMS-MWCNT composite [18], seems not to be a major factor for irreversible photomechanical response in RET-MWCNT composites.
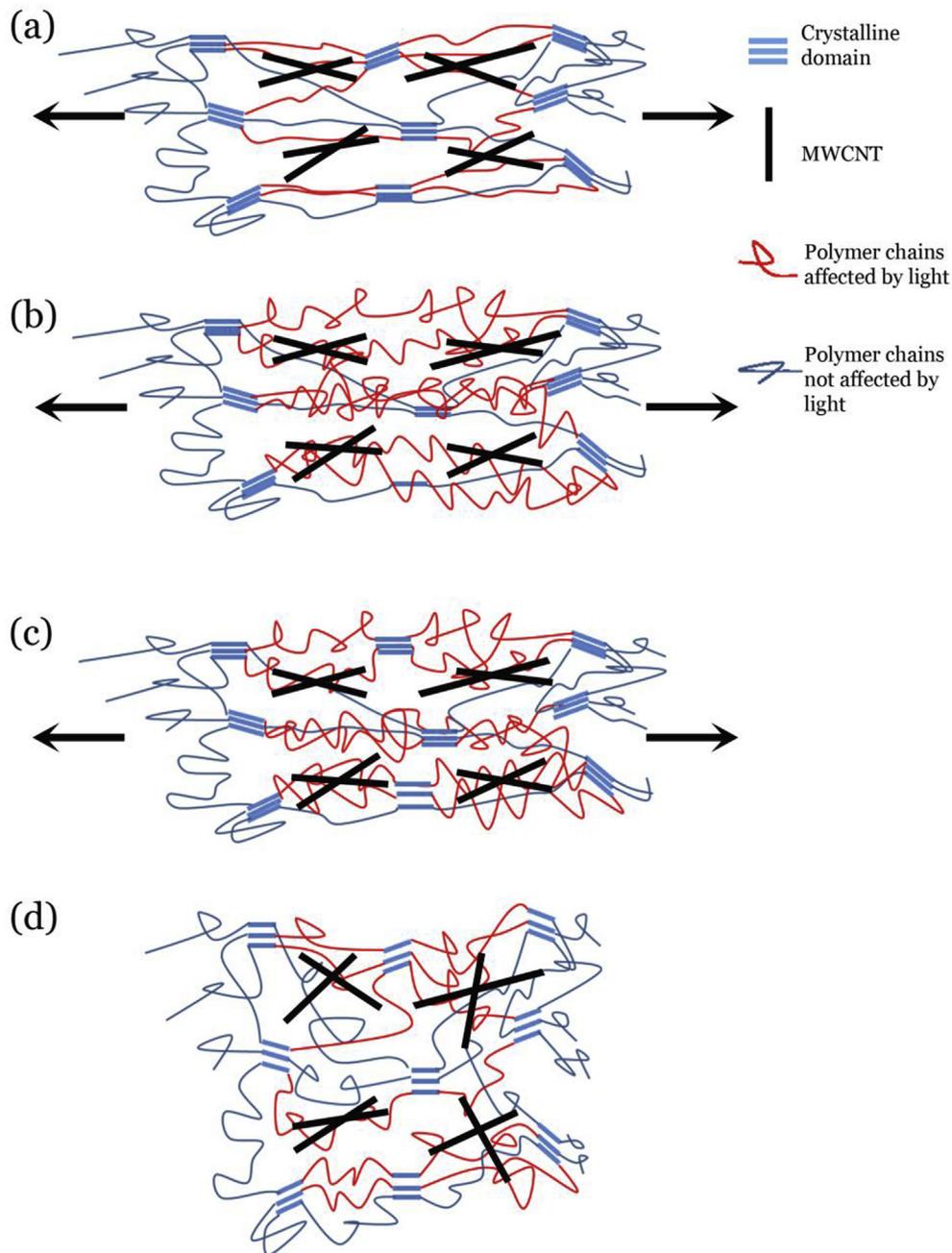
Fig. 6. Microscopic model for the photo-response in RET-MWCNT composite. (a) The composite subjected to a pre-strain. (b) Light irradiation induces melting of crystalline domains. (c) Recrystallized domains formed after removing the light irradiation and connect to the relaxed polymer chains again. (d) Plastic deformation exists in a freestanding RET-MWCNT composite.

Based on all the experimental observations, we propose the following microscopic model to explain the photomechanical response in the RET-MWCNT composite. In the RET itself, it has been shown that the constituent (i) epoxide group is for anchoring to functional groups onto the CNTs, while (ii) the butyl group processes a relative low glass transition temperature, which serves as a soft segment at ambient temperature and confers elastomeric properties and (iii) the ethylene group can undergo crystallization and forms thermally reversible physical crosslinks. The CNTs embedded in the RET can absorb light and covert it to thermal energy, which subsequently induce the melting of the crystalline domains. When pre-strains applied to the RET-MWCNT composite, polymer chains in the composite between crystalline domains are stretched (Fig. 6a). Upon the first light irradiation, the energy absorbed in the embedded MWCNTs melts the crystalline domains around them, as shown in Fig. 6b. Consequently, part of the polymer chains (marked in red) are released from the melted crystalline domains and the stresses will then be partially relaxed, leading to the observed irreversible stress relaxation. The rest of the polymer chains (marked in blue) remain being stretched due to the attachment to the crystalline domains. As the light irradiation is removed (Fig. 6c), the temperature in the RET matrix decreases and the previously melted crystalline domains can be recrystallized. The superior thermal conductivity of the matrix with percolating CNTs, as well as the intimate connection between RET and CNTs through the epoxide groups, is crucial in stress relaxation under the first light irradiation. In the subsequent light irradiation with the same intensity, the overall number of the melted crystalline domains remains constant. However, a higher light intensity may re-exhibit the stress relaxation response, by melting more crystalline domains that connect to the stretched polymer chains and release the stress. The particular structure of the RET, where ethylene group can undergo crystallization to form thermally reversible physical crosslinks and the epoxide group intimately connects to the CNTs, may also explain the lack of a similar irreversible response in PDMS-MWCNT composites.

One of the immediate predictions from the microscopic model is that after removing the external constraints, residual strain will exist in a freestanding RET-MWCNT composite after irradiation. Plastic deformation would arise due to different responses between the relaxed polymer chains affected by the light induced melting of crystalline domains (red in Fig. 6) and the unrelaxed polymer chains that are not affected by light irradiation (blue in Fig. 6). As indicated in Fig. 6d, the equilibrium between two types of polymer chains in a constraint free sample leads to plastic deformation. The prediction was verified experimentally, and is shown in Fig. 5b. After light irradiation at intensity of 97 mW/cm^2, the RET composites were cooled down to room temperature before removing from the grippers, which allows for the formation of the recrystallized domains. Considerable plastic deformation was observed in the composite. The residual strain (ε_{res}), which is defined as ratio between irreversible displacement and initial sample length, was found to be proportional to the pre-strain (ε). By assuming that the composite reached a quasi-equilibrium state after light irradiation, we can predict the residual strain based on the phenomenological relation of the number density of crystalline domains N (ε, I_e) by Equation (3). From this equation, the first term: $N_0 f(\varepsilon)$, is the number density of crystalline domains when pre-strain is applied, while the second term: $\alpha I_e f(\varepsilon) N_0$, represents the reduction of number density after light irradiation, and it is assumed to be equivalent to the number density of recrystallized domains. In the freestanding state, as the average stress should be zero, the equilibrium between the relaxed and unrelaxed polymer chains would imply:

$$N_0 f(\varepsilon)\alpha I_e k_B T(\varepsilon - \varepsilon_{res}) = N_0 f(\varepsilon)(1 - \alpha I_e)k_B T\varepsilon_{res}. \qquad (4)$$

Therefore, the residual strain is varying as $\varepsilon_{res} = \alpha I_e \varepsilon$. For a light intensity of 97 mW/cm^2, the prediction is plotted as a dashed line in Fig. 5b, which shows a good agreement with the experimental measurements.

Finally, we demonstrated the possibility of making a RET-MWCNT composite based mechanical actuator [49] as shown in Fig. 7. To achieve the bending response upon light irradiation, the composite was first subjected to 50% pre-strain and irradiated by visible light (of intensity 70 mW/cm^2) which induces a residual strain of around 25% and an initial bending angle of 18°. With a higher light intensity, a bending towards the direction of light irradiation was observed in a few second and increased rapidly at ~156 mW/cm^2. In the inset of Fig. 7, with I_e = 177 mW/cm^2, a large bending with an angle change of 16° is reached. Such mechanical actuation arises from the inhomogeneous contraction of the composite [50]. As the composite is subjected to a higher light intensity, more crystalline domains will be melted and allow the polymer chains to convert to a more coiled state to maximize the entropy [51–53]. Moreover, the differential heating along the thickness of the composite induces a thermal gradient aiding the bending response. Since the bending relies on the melting of the crystalline domains, which in turn is related to the irreversible light response in the composite, the bending is fixed when light irradiation is removed.

4. Conclusions

We have reported new photo-response characteristics, relative to a stretched RET-MWCNT composite, encompassing both irreversible and reversible stress modulations. Such dual responses were not observed in the PDMS-MWCNT composites. The individual and synergetic influence of the light intensity and the pre-strain were examined in detail. The transformation of crystalline domains to amorphous domains in the RET matrix was posited as the cause for the observed irreversible response. While the CNTs embedded in polymer matrix served to transduce the incident light irradiation to thermal energy and increase the temperature in both PDMS-CNT and RET-CNT composites, the intimate connection enabled by the epoxide-CNT linkages in the RET polymer was thought to facilitate to the irreversible response. A microscopic mechanical model incorporating the melting of crystalline domains as well as the release of the connected polymer chains was proposed to explain
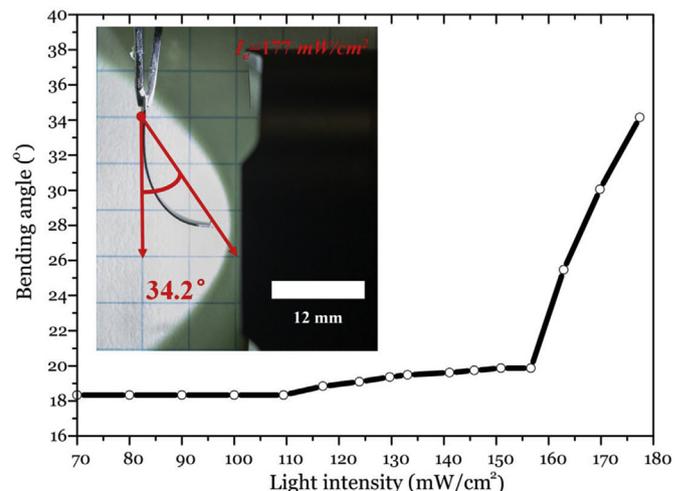

Fig. 7. Photo actuated bending in a RET-MWCNT composite beam.

the phenomena. The possibility of the RET-MWCNT composite for serving as a base material in mechanical actuation at a short time scale was probed, with possible application in light-mechanical energy transduction [54], *e.g.,* in robotics [2,4] Our studies also provide motivation for a deeper investigation of the role of individual polymer matrices and interfaces, when combined with filler elements such as CNTs, in energy absorption, conversion and transduction.

Acknowledgements

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.compositesb.2017.09.036.

References

[1] Lu S, Panchapakesan B. Photomechanical responses of carbon nanotube/polymer actuators. Nanotechnology 2007;18(30):305502.
[2] Ikeda T, Mamiya Ji, Yu Y. Photomechanics of liquid-crystalline elastomers and other polymers. Angew Chem Int Ed 2007;46(4):506–28.
[3] Higuchi M, Minoura N, Kinoshita T. Photoinduced structural and functional changes of an azobenzene containing amphiphilic sequential polypeptide. Macromolecules 1995;28(14):4981–5.
[4] Zhang X, Yu Z, Wang C, Zarrouk D, Seo J-WT, Cheng JC, et al. Photoactuators and motors based on carbon nanotubes with selective chirality distributions. Nat Commun 2014;5.
[5] Ahir S, Terentjev E, Lu S, Panchapakesan B. Thermal fluctuations, stress relaxation, and actuation in carbon nanotube networks. Phys Rev B 2007;76(16):165437.
[6] Koerner H, Price G, Pearce NA, Alexander M, Vaia RA. Remotely actuated polymer nanocomposites—stress-recovery of carbon-nanotube-filled thermoplastic elastomers. Nat Mater 2004;3(2):115–20.
[7] Landi BJ, Raffaelle RP, Heben MJ, Alleman JL, VanDerveer W, Gennett T. Single wall carbon nanotube-Nafion composite actuators. Nano Lett 2002;2(11):1329–32.
[8] Tahhan M, Truong V-T, Spinks GM, Wallace GG. Carbon nanotube and polyaniline composite actuators. Smart Mater Struct 2003;12(4):626.
[9] Mahimwalla Z, Yager KG, Mamiya J-i, Shishido A, Priimagi A, Barrett CJ. Azobenzene photomechanics: prospects and potential applications. Polym Bull 2012;69(8):967–1006.
[10] Yu Y, Nakano M, Ikeda T. Photomechanics: directed bending of a polymer film by light. Nature 2003;425(6954):145.
[11] Li Y, He Y, Tong X, Wang X. Photoinduced deformation of amphiphilic azo polymer colloidal spheres. J Am Chem Soc 2005;127(8):2402–3.
[12] Yu H, Ikeda T. Photocontrollable liquid-crystalline actuators. Adv Mater 2011;23(19):2149–80.
[13] Hugel T, Holland NB, Cattani A, Moroder L, Seitz M, Gaub HE. Single-molecule optomechanical cycle. Science 2002;296(5570):1103–6.
[14] Shabanian M, Basaki N. New photosensitive semi aramid/organoclay nanocomposite containing cinnamoyl groups: synthesis and characterization. Compos Part B Eng 2013;52:224–32.
[15] Eisenbach CD. Isomerization of aromatic azo chromophores in poly (ethyl acrylate) networks and photomechanical effect. Polymer 1980;21(10):1175–9.
[16] Tanchak OM, Barrett CJ. Light-induced reversible volume changes in thin films of azo polymers: the photomechanical effect. Macromolecules 2005;38(25):10566–70.
[17] Lee KM, Wang DH, Koerner H, Vaia RA, Tan LS, White TJ. Enhancement of photogenerated mechanical force in azobenzene-functionalized polyimides. Angew Chem 2012;124(17):4193–7.
[18] Ahir SV, Terentjev EM. Photomechanical actuation in polymer–nanotube composites. Nat Mater 2005;4(6):491–5.
[19] Lu H, Yao Y, Huang WM, Leng J, Hui D. Significantly improving infrared light-induced shape recovery behavior of shape memory polymeric nanocomposite via a synergistic effect of carbon nanotube and boron nitride. Compos Part B Eng 2014;62:256–61.
[20] Koo Y, Littlejohn G, Collins B, Yun Y, Shanov VN, Schulz M, et al. Synthesis and

characterization of Ag–TiO 2–CNT nanoparticle composites with high photocatalytic activity under artificial light. Compos Part B Eng 2014;57:105–11.
[21] Fan X, Khosravi F, Rahneshin V, Shanmugam M, Loeian M, Jasinski J, et al. MoS2 actuators: reversible mechanical responses of MoS2-polymer nanocomposites to photons. Nanotechnology 2015;26(26):261001.
[22] Zhang Y, Iijima S. Elastic response of carbon nanotube bundles to visible light. Phys Rev Lett 1999;82(17):3472.
[23] Lu S, Ahir SV, Terentjev EM, Panchapakesan B. Alignment dependent mechanical responses of carbon nanotubes to light. Appl Phys Lett 2007;91(10):103106.
[24] Courty S, Mine J, Tajbakhsh A, Terentjev E. Nematic elastomers with aligned carbon nanotubes: new electromechanical actuators. EPL Europhys Lett 2003;64(5):654.
[25] Ahir S, Terentjev E. Fast relaxation of carbon nanotubes in polymer composite actuators. Phys Rev Lett 2006;96(13):133902.
[26] Kong K, Mariatti M, Rashid A, Busfield J. Enhanced conductivity behavior of polydimethylsiloxane (PDMS) hybrid composites containing exfoliated graphite nanoplatelets and carbon nanotubes. Compos Part B Eng 2014;58:457–62.
[27] Ahir S, Squires A, Tajbakhsh A, Terentjev E. Infrared actuation in aligned polymer-nanotube composites. Phys Rev B 2006;73(8):085420.
[28] Love C, Karbhari V. Filled reactive ethylene terpolymer primers for cathodic disbondment mitigation. J Appl Polym Sci 2008;110(3):1531–44.
[29] Love CT, Xian G, Karbhari VM. Cathodic disbondment resistance with reactive ethylene terpolymer blends. Prog Org Coatings 2007;60(4):287–96.
[30] Tasis D, Tagmatarchis N, Bianco A, Prato M. Chemistry of carbon nanotubes. Chem Rev 2006;106(3):1105–36.
[31] Love C, Gapin A, Karbhari V. Interfacial adhesion in multi-walled carbon nanotube/reactive ethylene terpolymer composites. Baltimore, MD: Society for the advancement of material and process engineering (SAMPE); 2007.
[32] Love C, Gapin A, Karbhari V. Multi-walled carbon nanotube reactive thermoplastic composite adhesives. In: 1st international conference on nano-polymers Berlin, Germany; 2007.
[33] Loomis J, Panchapakesan B. Dimensional dependence of photomechanical response in carbon nanostructure composites: a case for carbon-based mixed-dimensional systems. Nanotechnology 2012;23(21):215501.
[34] Park O-K, Chae H-S, Park GY, You N-H, Lee S, Bang YH, et al. Effects of functional group of carbon nanotubes on mechanical properties of carbon fibers. Compos Part B Eng 2015;76:159–66.
[35] Park S-H, Yun D-J, Theilmann P, Bandaru P. Superior electrical and mechanical characteristics observed through the incorporation of coiled carbon nanotubes, in comparison to non-coiled forms, in polymers. Polymer 2013;54(4):1318–22.
[36] Love C, Xian G, Karbhari V. Thermal, mechanical, and adhesive properties of HDPE/reactive ethylene terpolymer blends. J Appl Polym Sci 2007;104(1):331–8.
[37] Wunderlich B, Poland D. Thermodynamics of crystalline linear high polymers. II. The influence of copolymer units on the thermodynamic properties of polyethylene. J Polym Sci Part A General Pap 1963;1(1):357–72.
[38] Polacco G, Stastna J, Vlachovicova Z, Biondi D, Zanzotto L. Temporary networks in polymer-modified asphalts. Polym Eng Sci 2004;44(12):2185–93.
[39] Bonart R. Thermoplastic elastomers. Polymer 1979;20(11):1389–403.
[40] Spontak RJ, Patel NP. Thermoplastic elastomers: fundamentals and applications. Curr Opin colloid & interface Sci 2000;5(5):333–40.
[41] Pfeifer S, Park S-H, Bandaru P. Analysis of electrical percolation thresholds in carbon nanotube networks using the Weibull probability distribution. J Appl Phys 2010;108(2):024305.
[42] Mondal S, Ganguly S, Das P, Khastgir D, Das NC. Low percolation threshold and electromagnetic shielding effectiveness of nano-structured carbon based ethylene methyl acrylate nanocomposites. Compos Part B Eng 2017;119:41–56.
[43] Matsuoka S. Relaxation phenomena in polymers. Hanser Munich etc; 1992.
[44] Treloar LRG. The physics of rubber elasticity. USA: Oxford University Press; 1975.
[45] Blanchard A, Parkinson D. Breakage of carbon-rubber networks by applied stress. Ind Eng Chem 1952;44(4):799–812.
[46] Bueche F. Mullins effect and rubber–filler interaction. J Appl Polym Sci 1961;5(15):271–81.
[47] Bueche F. Molecular basis for the Mullins effect. J Appl Polym Sci 1960;4(10):107–14.
[48] Mullins L. Softening of rubber by deformation. Rubber Chem Technol 1969;42(1):339–62.
[49] Bouhamed A, Müller C, Choura S, Kanoun O. Processing and characterization of MWCNTs/epoxy nanocomposites thin films for strain sensing applications. Sensors Actuators A Phys 2017;257:65–72.
[50] Yang W, Wang X, Fang C. Pull-in instability of carbon nanotube-reinforced nano-switches considering scale, surface and thermal effects. Compos Part B Eng 2015;82:143–51.
[51] Long KN, Scott TF, Qi HJ, Bowman CN, Dunn ML. Photomechanics of light-activated polymers. J Mech Phys Solids 2009;57(7):1103–21.
[52] Lendlein A, Jiang H, Jünger O, Langer R. Light-induced shape-memory polymers. Nature 2005;434(7035):879–82.
[53] Scott TF, Schneider AD, Cook WD, Bowman CN. Photoinduced plasticity in cross-linked polymers. Science 2005;308(5728):1615–7.
[54] Behl M, Lendlein A. Shape-memory polymers. Mater today 2007;10(4):20–8.