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Citation

SLOBODIAN, Petr, Pavel ŘÍHA, Robert OLEJNÍK, and Jiří MATYÁŠ. Electrothermal actuation and release of adhesiveness of conductive carbon nanotube/epoxy composites by Joule heating. *Macromolecular Symposia* [online]. vol. 405, iss. 1, John Wiley and Sons Inc, 2022, [cit. 2024-02-01]. ISSN 1022-1360. Available at https://onlinelibrary.wiley.com/doi/10.1002/masy.202100267

DOI

https://doi.org/10.1002/masy.202100267

Permanent link

https://publikace.k.utb.cz/handle/10563/1011192

Electrothermal Actuation and Release of Adhesiveness of Conductive Carbon Nanotube/Epoxy Composites by Joule Heating

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The effect of an embedded electro-conductive multi-walled carbon nanotube (MWCNT) nanopaper in an epoxy matrix on the release of the frozen actuation force and the actuation torque in the carbon nanotube nanopaper/epoxy composite after heating above its glass transition temperature is assessed. The presence of the nanopaper augments the recovery of the actuation stress by the factor of two in comparison with the pure epoxy strip. The strengthening of the composite is attributed to the interlocking of the carbon nanotubes with the epoxy. Moreover, the internally heated electro-conductive carbon nanotube nanopaper/epoxy composite not only substantially shortens curing time while retaining comparable strength of the adhesive bonding of the steel surfaces but also enables a release of such bonds by repeated application of DC current.

Keywords: Actuation force, epoxy nanocomposites, glass transition, Joule heating

1. Introduction

Recently, the progress in shape memory epoxies and their carbon nanotube composites has been reviewed.[**1**] However, the interaction of the carbon nanotube structure with the epoxy molecular system is not fully known yet and is not mentioned in ref.[**1**] or in the extensive review.[**2**] Here, we show how a carbon nanotube nanopaper/epoxy composite modulates the release of the frozen actuation force during its Joule heating, analyze the electrothermal actuation controlled by heating, and introduce efficient adhesive bonding of metals by this composite.

2. Results

To assess a strengthening mechanism of the electrothermal actuation in the multi-walled carbon nanotube ($MWCNT$) nanopaper/epoxy composite, the extended composite and the epoxy strip were cooled down from 75 °C to the ambient temperature of 25 °C and then reheated to the rubbery state at 75 °C at the rate 2.7 and 3.3 °C s^{-1}, respectively. When the strips were heated again over the glass transition temperature T_g, equal to 53.9 and 35.1 °C for the composite and the pure epoxy, respectively, the actuating stress started to increase at the T_g as the raising temperature gradually released frozen arrangements of the epoxy crosslinked structure and concurrently longitudinally stretched the nanotube structure of the $MWCNT$ nanopaper. The actuating stress in the composite strip equal to the difference between the minimum and the maximum stress values plotted in **Figure 1** was 1.5 MPa after their initial deformation of 2.71%. The analogous stress in the epoxy strip was 0.57 after the initial deformation of 2.42%. Since the T_g temperature of 35.1 °C was exceeded in about 3 s after the start of heating, the stress in the epoxy strips regained rapidly. On the other hand, actuating in the composite strips proceeded slightly slower, since the T_g temperature of 53.9 °C was not exceeded until 8 s after the start of heating.

The electrothermal actuation stress in the composite strip was two-times higher than the actuation stress in the epoxy strip at the corresponding pre-deformation. The embedded nanopaper thus manifested as the reversibly elastically deformable element with a strong interlocking into an epoxy matrix responsible for the increase of the actuation force in the $MWCNT$ nanopaper/epoxy composite.

The other example of the actuation test consisted of straightening the bent $MWCNT$ nanopaper/epoxy composite strip. After lheating above T_g, the straight strips were bent at a right angle and cooled to the room temperature. When the bent strip was reheated by Joule heating with an electric current of different actuating voltages, the bent strip restored to some degree its original straight shape (**Figure 2**). A shape change was enumerated as a straightening ratio S_r (%) $= (\alpha_i - \alpha_f)/\alpha_i$ × 100, where ai denotes the initial bending angle (90°) and af the final bending angle.

At the final transformation temperature of 76.2 °C the straightening of the bent strip to the straightened one ($S_r = 100\%$) was achieved in about 43 s. At 47.1 °C, that is, at the temperature below T_g (53.6 °C), the final unbent angle was 64° and the maximum S_r 29% only was achieved in about 600 s.

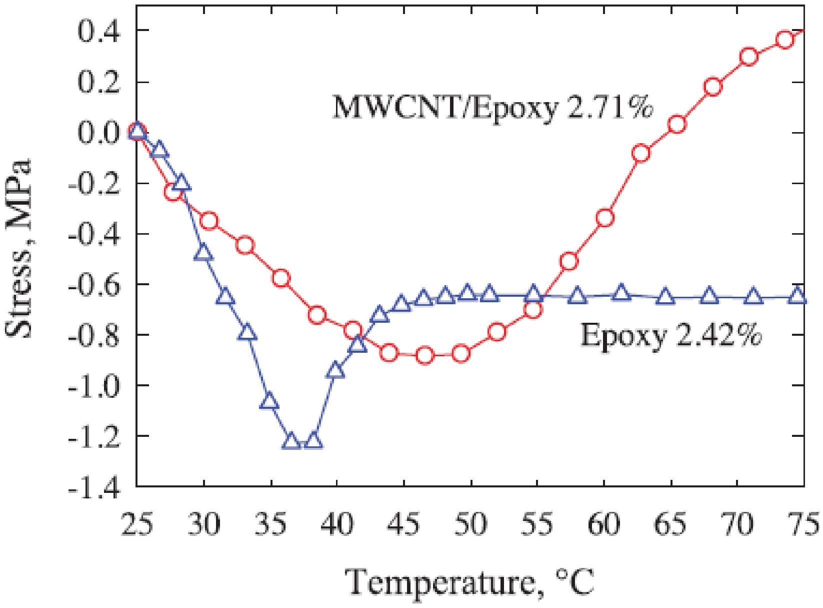

Figure 1. Temperature dependence ofthe actuating stress during heating ofthe multi-walled carbon nanotube ($MWCNT$) nanopaper/epoxy (red circles) and epoxy (blue triangles) strips from the temperature of 25C to 75 °C at the fixed comparable pre-strain 2.71% and 2.42%, respectively.

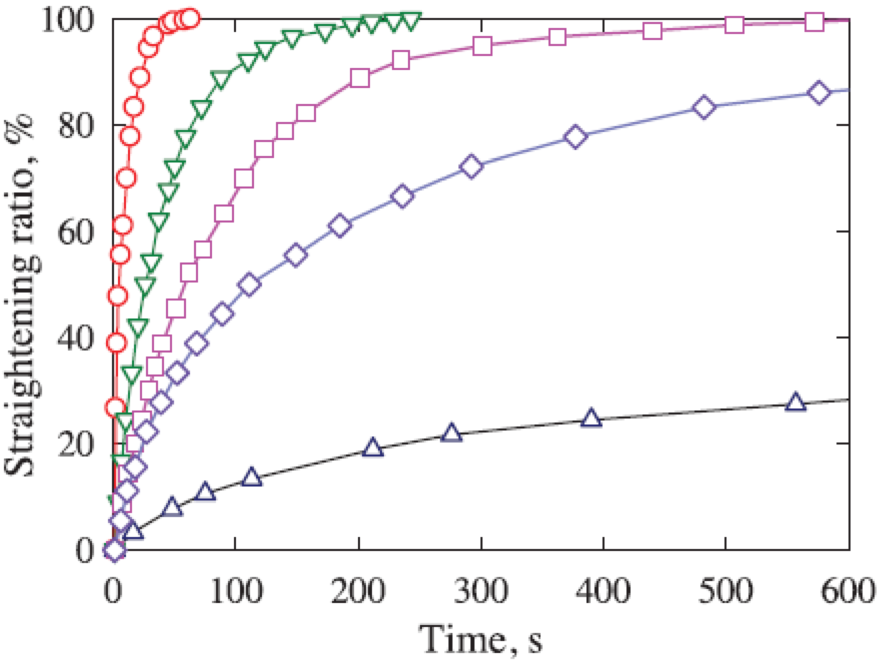

Figure 2. The dependence of the strip straightening ratio on time in the course of Joule heating by 7.5 V from the temperature of 25 °C to 76.2 °C (red circles), to 63.6 °C by 6.5 V (green triangles down), to 58.5 °C by 6 V (pink squares), to 55 °C by 5.5 V (blue diamonds), and to 47.1 °C by 4.5 V (dark blue triangles).

The release of the actuation force in the composite depends on the release of frozen polymer epoxy segments. A more elastic composite, which requires a greater stress to deform, indicates a strong interlocking of nanopaper into an epoxy matrix. In the course of setting of a temporary shape of a rubbery epoxy strip, the segments between chemical crosslinks adapt to the external stretching load and elongate.[**1**] It results in a longitudinal orientation of most of the segments and a dislocation of crosslinked points.[**3**] Upon cooling and maintaining the deformed shape, secondary crosslinks are formed among the orientated segments. These secondary crosslinks are the main principle of the fixation of the molded shape.[**4**] After a reheating above T_g, the shape recovery is initiated by detaching of the secondary crosslinks and releasing of the stored strain energy.

Rapidly and uniformly heated $MWCNT$/epoxy composite strips by Joule heating can also be used to bond components. To test this technique, we used two zinc coated steel strips (length 100 mm, width 10 mm, thickness 0.5 mm, overlap 10 mm, overlapping area 100 mm2) and inserted $MWCNT$ nanopaper between them filled with uncured epoxy resin. The bonding of the steel strips occurred within 5 min after Joule heating by DC electric power 6 W at the temperature about 160 °C.

According to results in **Figure 3**, the test of the adhesive strength of the bonding of the steel strips gave the ultimate shear stress values of 19.4 N mm^{-2}. The $MWCNT$/epoxy composite achieved a comparable strength of bonding yet the required curing time was considerably shorter than when the conventional epoxy adhesive is used. Moreover, the bonding retained its electrical conductivity and thus was able to be further modulated by the Joule heating. Once the temperature of the $MWCNT$ nanopaper/epoxy composite, which glued together the steel strips, reached 72 °C within about 1 min, the bond of the steel strips was released at the ultimate shear stress of 1.2 N mm^{-2}. Hence, the bond of the steel strips, which overlapped 100 mm^2 and could withstand a total adhesive force of 1940 N that is equivalent to about 200 kg of load under gravity, could be released by force 120 N or about 12 kg of load under gravity, which can be readily exerted by human hand.

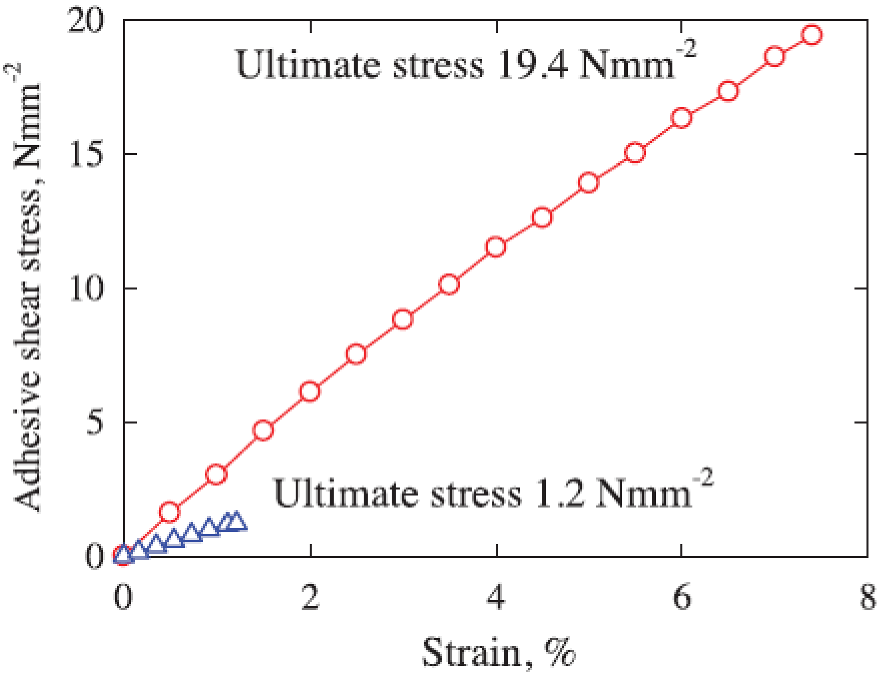

Figure 3. The shear stress-strain relations for the bonded steel strips using the multi-walled carbon nanotube ($MWCNT$) nanopaper/epoxy composite (red circles) and for the reheated adhesive bonding by the $MWCNT$ nanopaper/epoxy composite at temperature 72 °C (blue triangles). The respective ultimate stress and ultimate strain values are inserted into the figure.

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3. Conclusions

We proposed a measurement that allowed us to assess and analyze the strengthening mechanism of the electrothermal actuation using Joule heating $MWCNT$/epoxy composite. We found that the regained actuation stress in the composite strips was two-times higher than the similar stress in the pure epoxy strips. This was because the more elastic structure of the stretched mutually intertwined epoxy segments and nanotubes of the nanopaper released when reheated a greater actuation stress than the less elastic stretched network of crosslinked segments of the pure epoxy.

4. Experimental Section

To make an $MWCNT$ nanopaper from pristine nanotubes (Sun Nanotech Co. Ltd., China), the nanotubes were deposited on a porous polyurethane electrospun non-woven membrane by a vacuum filtration. The two-component epoxy resin Epox G 200 (Davex Chemical s.r.o., Prague, Czech Republic) was used. The component A was an epoxy resin prepolymer (hydrogenated bisphenol A polymer with epichloro-hydrin [CAS: 30583-72-3]). The component B (trimethylolpropane tris [poly(propylene glycol), amine terminated] ether [CAS: 39423-51-3]) was a curing agent. To prepare the electroconductive $MWCNT$ nanopaper/epoxy composite strip (40 x 20 mm), at first were two Cu strip electrodes glued at the opposite sides of the about 300 μm-thick nanopaper. Next, the porous nanopaper was laid on a polytetrafluorethylene foil and its pores were filled up with ca. 0.2 mL of the above-described epoxy resin and curing agent at the A/B ratio 100:75 and cured by Joule heating at temperature around 60 °C for 15 min. Further details ofthe experimental procedures were similar to those in our previous articles.[**4**,**5**]

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