

Carbon Nanotube Rubber Stays Rubbery in Extreme Temperatures**

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carbon nanotubes · chemical vapor deposition · rubber · temperature invariance · viscoelasticity

A rubbery material can undergo elastic deformation under stress and return to its original shape upon removal of the deforming force. This behavior of elastic deformation and recovery is known as rubbery elasticity or viscoelasticity,^[1] and gives rise to rubbery materials for various applications, ranging from household (rubber bands and balloons, gloves, pencil erasers, shoe soles, carpets) to industrial products (adhesives, door and window profiles, hoses, tires). Viscoelastic properties are temperature-dependent and none of the existing elastomers can retain their viscoelasticity over a wide temperature range.^[1] The most thermally resistant silicone rubber hardens at -55°C and degrades at 300°C .^[2]

Recently, Hata and co-workers at the AIST and JST in Japan developed new viscoelastic material from carbon nanotubes (Figure 1) that is similar to silicone rubber, but



Figure 1. Photograph of the flexible CNT rubbery materials developed by Xu et al. Inset: SEM image of the area marked in the photograph. Adapted from Ref. [3].

maintains temperature-invariant viscoelasticity from -196 to 1000°C in an oxygen-free environment.^[3] Among many other applications, therefore, such a temperature-invariant rubbery material made from carbon nanotubes (CNT rubber) could be

used as dampeners (antivibration mounts) for high-vacuum furnaces and even aerospace vehicles that travel to the cold interstellar space.

Viscoelasticity is a behavior that is not specific to rubber. In fact, all macromolecules exhibit viscoelasticity above their softening temperatures.^[1] Because of the coil structure, both the movement of chain segments within one coil and the movement of entire coils with respect to each other are possible for macromolecules. Near the softening point, the chain segments become mobile and the material slowly changes its shape under the influence of a deformation force.^[1,4] Further temperature increase causes more and more segmental contacts within and between coils to be removed, and the “thawed-out” chain segments become more and more mobile. Thus, a considerable deformation, such as stretching of the polymeric material, is possible even with a relatively small deformation force (Figure 2).^[4]

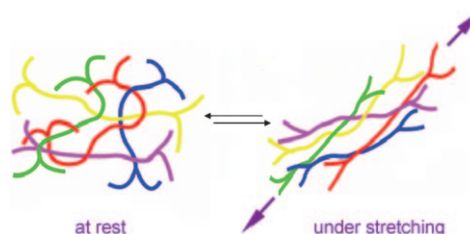


Figure 2. The viscoelastic deformation of polymers in the rubber-elastic state. Adapted from Ref. [4].

If there are sufficient intramolecular and/or intermolecular segmental links remaining at a certain temperature, however, macromolecular coils will subject to a deformation but not move with respect to each other. Therefore, the coils resume their most probable form and the stretched material returns to its original shape as soon as the deforming force is removed (Figure 2). As the thermally induced macromolecular motion described above is responsible for viscoelasticity, the viscoelastic properties of existing elastomers are inherently temperature-dependent.^[1,4]

Having a conjugated all-carbon structure with an elongated molecular symmetry, small-diameter carbon nanotubes (CNTs) show certain polymeric features.^[5] Unlike traditional polymeric elastomers, however, the CNT rubber reported by Xu et al.^[3] is an unusual viscoelastic material with temper-

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ature-invariant viscoelasticity at temperatures as low as -196°C and as high as 1000°C . These authors used a combination of reactive ion etching (RIE) to reduce the catalyst density and water-assisted chemical vapor deposition (CVD)^[6] to grow very clean (99.9%), long (4.5 mm) strands of single-, double, and triple-walled CNTs. CNTs in the material developed by Xu et al.^[3] were found to randomly tangle (Figure 3a at 0% shear strain) in a way similar to polymer chains in traditional elastomers (Figure 2, left), forming numerous short contacts with one another (Figure 3d). Upon heating or under stress (Figure 3c), the energy goes into overcoming the large van der Waals attraction^[7] between the CNTs, resulting in an unzipping of the contact points (Figure 3e, top). However, no energy is required for zipping (Figure 3e, top), leading to an elastic shape recovering when the stress/heat is removed. Xu et al.^[3] have reversibly stretched their CNT rubber in the direction of applied stress up to 5% strain before an irreversible process of straightening, slipping, and bundling of CNTs occurred (Figure 3c) at the failure strain of 100% (Figure 3b, bottom). The viscoelastic behavior of the CNT rubber is similar to that of silicone rubber (cf. Figure 2). Unlike silicone rubber, which is brittle when cold and breaks down at high temperatures, the newly-developed CNT rubber remains flexible over a wide temperature range (between -196°C and 1000°C) with a temperature-invariant viscoelasticity (Figure 3b). Further-

more, it is envisaged that the CNT rubber can be made more elastic, stronger, or softer by varying the nanotube density.

In the study by Xu et al.,^[3] the authors attributed the observed unusual thermal stability to multilevel structural features characteristic of the CNT rubber and its constituent nanotubes. First, the porous network structure (Figure 3a), coupled with excellent thermal transport properties intrinsically associated with CNTs,^[8] allows the CNT rubber for rapid and efficient heat dissipation to prevent significant heat accumulation. Second, additional energy dissipation occurs as the CNTs zip and unzip at points of contact (Figure 3e, top). The energy which is required to overcome the large van der Waals attraction between each of the CNT contacts during the zipping and unzipping process is insensitive to temperature, leading to the observed temperature-invariant viscoelasticity (Figure 3b). This viscoelasticity is further enhanced by the deformation of individual CNTs from flattening to recovery (Figure 3e, bottom) as the collapsed state for small nanotubes with inner diameters of 3–5.5 nm is metastable.^[9] Last, but not the least, the absence of catalyst residue in the material produced by the combined RIE-CVD^[6] can significantly reduce the oxidative degradation of nanotube structures, and hence the excellent thermal stability for the CNT rubber.

Owing to its unusual thermal stability and temperature-invariant viscoelasticity, the CNT rubber developed by Xu et al.^[3] could find applications in extremely hot or cold

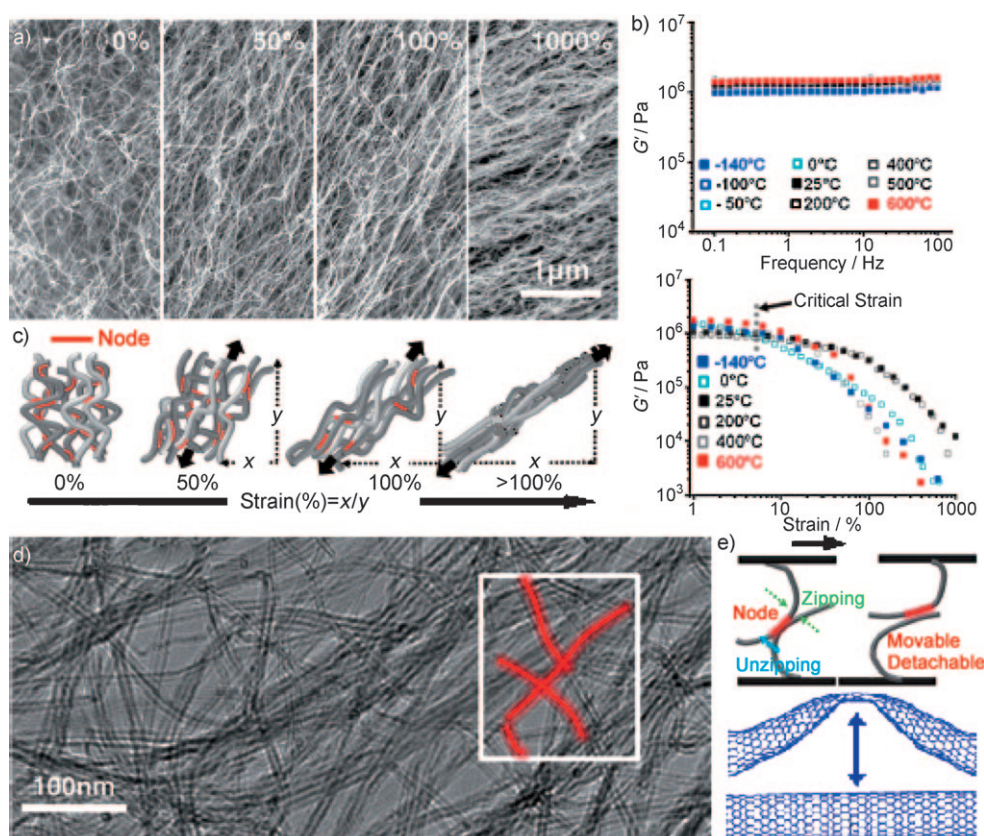


Figure 3. a) SEM images at varying shear strains. b) Storage modulus G' of the CNT rubber as function of frequency (0.1 to about 100 Hz; upper plot) and strain amplitude (1 to about 1000%; lower plot) at temperatures from -140°C to 600°C . c) The change in intertube structure with strain (see also Figure 2). d) TEM image of the as-prepared intertube structure. Nodes are indicated in the marked region. e) Zipping and unzipping of nodes (top) and the flattening and recovery deformation of nanotubes (bottom). Adapted from Ref. [3].

environments. However, possible short-term applications at a high temperature would be limited to a vacuum or air-tight working environment, as most small-diameter nanotubes burn in air above about 400°C. Other applications may require more elastic CNT rubbers, with an increased maximum strain ($> 5\%$) and/or the failure strain ($> 100\%$), for reversible structural changes over a relatively large deformation. Although some properties of the CNT rubber still need to be further improved for certain applications, the pioneering work reported by Xu et al.^[3] has clearly revealed the versatility of clever syntheses for producing CNT rubbery materials with exotic viscoelastic properties to outperform the existing elastomers. Continued research efforts in this embryonic field could give birth to a flourishing area of specialty CNT elastomers of practical significance.

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