

Temperature-Activated Interfacial Friction Damping in Carbon Nanotube Polymer Composites

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ABSTRACT

Effect of temperature on interfacial sliding in single-walled carbon nanotube polycarbonate composites is investigated experimentally. We show that interfacial slip at the tube–polymer interfaces can be activated at relatively low dynamic strain levels ($\sim 0.35\%$) by raising temperature to $\sim 90^\circ\text{C}$. We attribute this to increased mobility of the polymer chain backbones at elevated temperatures and thermal relaxation of the radial compressive stresses at the tube–polymer interfaces. These results show the potential of polymer nanocomposites as high-temperature damping materials for vibration and acoustic suppression in a variety of dynamic systems.

The demand for high-performance damping materials is rapidly and continuously growing in a variety of aerospace, mechanical, and civil systems. Although viscoelastic polymer based damping treatments¹ are shown to be promising for vibration and noise control, they suffer from several limitations such as high weight penalty, compactness issues, poor reliability, low thermal conductivity, and poor performance at elevated temperatures. For these reasons there is a need to develop advanced damping materials that can overcome the limitations discussed above.

In recent years, several groups^{2–6} have explored the potential of using carbon nanotube fillers to inject damping into composite structures. The combination of extremely large interfacial contact area, high aspect ratio, and low mass density implies that interfacial sliding of nanotube fibers within a polymer or epoxy matrix has the potential to cause significant dissipation of energy with minimal weight penalty. Another attractive feature of this concept is that the nanoscale inclusions could potentially be seamlessly integrated within composite/heterogeneous systems without sacrificing mechanical properties or structural integrity. Our group first demonstrated² that interfacial tube–tube sliding within clusters of multiwalled carbon nanotubes (MWNTs) could be used for damping enhancement. However the required loading fraction of nanotubes was quite high ($\sim 50\%$) since the weak van der Waals interaction between the nanotubes was not effective at dissipating energy. Subsequently we

explored the tube–matrix sliding energy dissipation mechanism and showed that up to 1000% increase³ in loss modulus of a polymer matrix can be achieved with relatively small (1–2%) weight fraction of oxidized single-walled carbon nanotube (SWNT) fillers. Wang and co-workers^{4,5} have also studied the damping properties of epoxy films with well-dispersed SWNT fillers and have also shown that the nanotube–polymer slip mechanism is far more effective at dissipating energy than one based on nanotube–nanotube sliding. In addition, Jalili and co-workers⁶ have recently shown impressive damping increases in epoxy resins by using SWNT fillers. The common feature in all of the above investigations was that they were performed at room temperature and the room-temperature damping response of the nanocomposite showed strong sensitivity to the strain amplitude. This is because to activate interfacial sliding of nanotubes the interfacial shear stress at the tube–polymer interfaces must exceed a critical or threshold value. Below this critical stress level, nanotube debonding does not take place and the loss modulus of the nanocomposite is similar to the pure polymer. Above the critical stress, the tube–matrix interfaces fail and frictional sliding is activated resulting in a dramatic increase in loss modulus (energy dissipation). The critical stresses needed to bring about nanotube–matrix interfacial slip depend on the polymer chemistry and the nanotube surface treatment, but for most polymers the critical stresses^{7,8} are in the 50–150 MPa range. In a recent study³ we showed that the dynamic strain amplitude needed to create such large interfacial shear stresses is close to the elastic limit of typical polymers (1–

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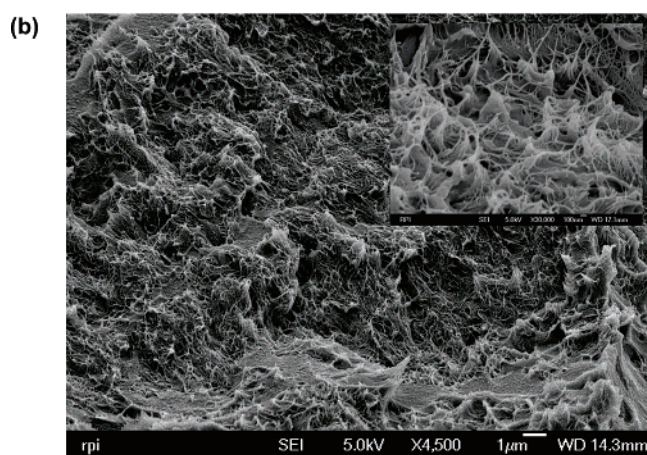
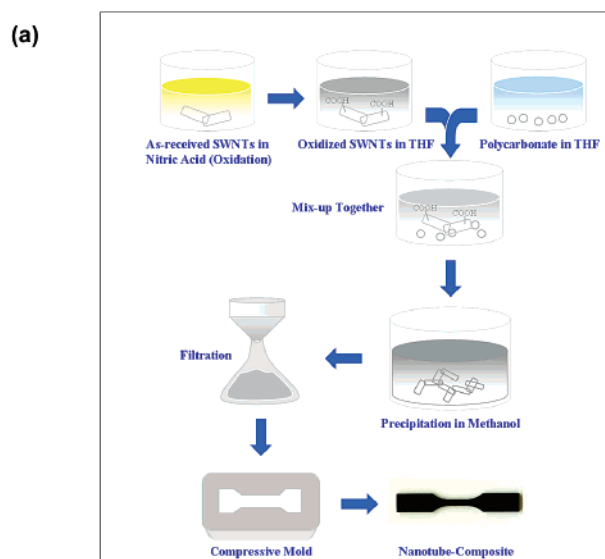


Figure 1. Fabrication of nanocomposite samples: (a) Schematic of the solution-mixing technique used for dispersing oxidized SWNT in the polycarbonate matrix. (b) Scanning electron microscopy (SEM) image of the fracture surface on the nanocomposite showing uniform dispersion of SWNT ropes in the polycarbonate matrix. The SWNT weight fraction for this case is 1.5%. Inset shows high magnification image of the SWNT ropes; the average rope diameter is ~ 35 nm.

1.5% range). In practice such large strains are unlikely to be encountered, and so it is important to investigate whether interfacial slip in nanotube composites can be activated at lower strain levels. In this paper we show that temperature can be used to facilitate nanotube–matrix interfacial slip at relatively low strain amplitudes. This work represents the very first report in the literature where the effect of temperature on the interfacial damping properties of carbon nanotube polymer composites has been characterized. The following sections will describe the fabrication protocols that were used to prepare the nanocomposites, the test procedure, and some of our key test results.

We used a solution mixing process (Figure 1a) to disperse single-walled carbon nanotubes (Hipco SWNT) in a polycarbonate (Lexan 121) matrix. Prior to dispersion the as-received SWNTs were oxidized^{9,10} by sonication in nitric acid. The resulting carboxylic groups on the SWNT help to exfoliate the nanotube bundles, and also the intermolecular

forces caused by dipole–dipole interaction between polar groups (i.e., carboxylic acid groups on the sidewall of nanotubes and the polar carbonate groups along polycarbonate chains), lead to better quality³ of dispersion. The oxidized SWNTs without further purification were first sonicated in a tetrahydrofuran (THF) solution and polycarbonate was dissolved separately in THF, followed by mixing them together in a ratio that resulted in the required nanotube concentration in the polymer. The mixture was sonicated (Sonics VC750, 750W, 20 kHz) for 15 min and was poured dropwise into methanol (methyl alcohol, anhydrous), which is an antisolvent for polycarbonate in a ratio of 1:5 between THF and methanol. The composite precipitated immediately, and the precipitate was filtered from the mixture and dried out (overnight) under vacuum in order to get rid of any remaining solvent or humidity. Then, the composites in the mold were hot pressed to prepare the standard tensile specimens, using a hydraulic press (CARVER No. 4122), which was preheated to 205 °C. The samples (Figure 1a) have dimensions of 3.2 mm (width), 3.0 mm (thickness), and 63.25 mm in length. Baseline polycarbonate samples (without nanotube fillers) of the same dimensions were also prepared following the same protocol. Figure 1b shows typical scanning electron microscopy (SEM) images of the fracture surface for SWNT–PC composite with 1.5% weight fraction of oxidized SWNTs. As seen in the SEM images, small bundles of SWNT are well dispersed in the polymer matrix. Each SWNT bundle is approximately 35 nm in diameter and appears to be coated with a polymer layer.

The nanocomposite and the baseline polymer samples were tested under dynamic cyclic loading in the uniaxial direction using an MTS-858 servo-hydraulic test facility. The test temperature was varied from -60 to 90 °C, using an MTS 651.05E environmental chamber. For each data point, the desired test temperature was maintained for at least 10 min prior to the application of the dynamic cyclic loading. The time-dependent strain and stress responses were measured using an MTS 632.26E-20 extensometer and the load cell of MTS-858 system, respectively. Two built-in thermocouples inside the environment chamber were used to monitor the test temperature. To characterize and quantify the damping behavior, the storage modulus and loss modulus of the nanocomposite as well as the baseline polycarbonate samples were calculated¹¹ using the measured uniaxial stress and corresponding strain responses. Several samples were tested to check for reproducibility, and the average and standard deviations for the complex modulus of the nanocomposite and baseline polycarbonate samples are presented in Figures 2–4.

Figure 2 illustrates the room temperature (~ 25 °C) behavior of the nanocomposite and baseline (pure) polycarbonate samples. The weight fraction of oxidized SWNT in our tests was selected as 1.5%. For higher nanotube loading fractions it was difficult to maintain good dispersion quality of the nanotubes in the polycarbonate matrix. Figure 2a indicates that the elastic modulus (or stiffness) of the nanocomposite shows a gradual decrease with increasing strain amplitude, suggesting that as the strain amplitude is

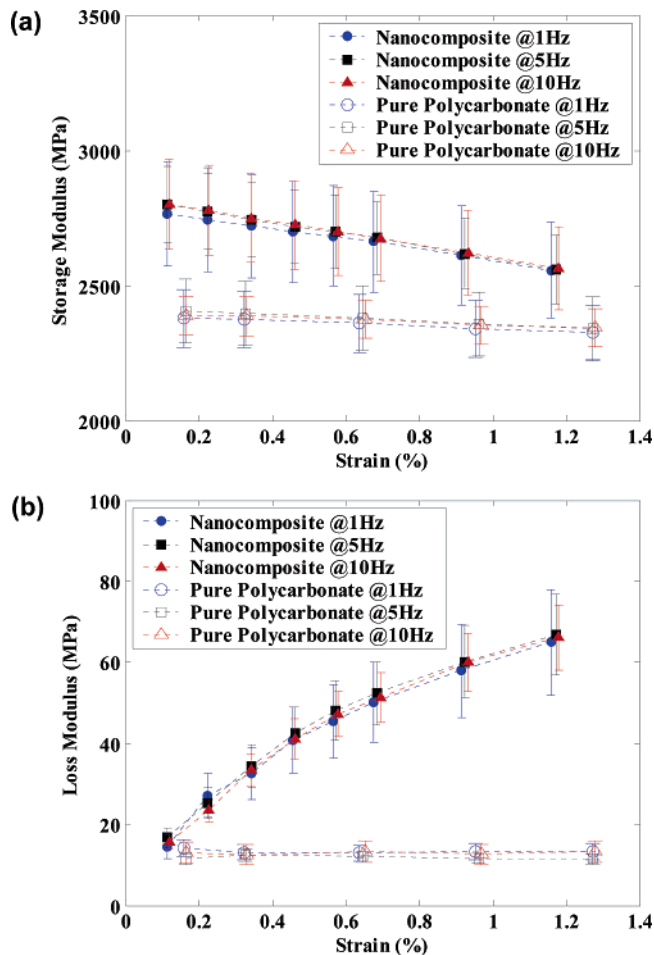


Figure 2. Viscoelastic characterization at room temperature. (a) Storage moduli of nanocomposite and pure polycarbonate as a function of strain amplitude and test frequency. The weight fraction of oxidized SWNT in the composite is 1.5%. The decrease of the storage modulus with increasing strain amplitude for the nanocomposite sample is indicative of interfacial slip at the SWNT-matrix interfaces. (b) Loss moduli of nanocomposite and pure polycarbonate as a function of strain and test frequency. The pure polycarbonate sample shows strain-independent damping behavior. In contrast the damping response of the SWNT-PC nanocomposite increases with strain amplitude which suggests the activation of tube-matrix interfacial slip at the higher strain amplitudes. In the 1–10 Hz frequency range, both samples show frequency-independent behavior for the storage and loss moduli.

increased the critical stress for nanotube-polymer interfacial slip is reached and filler-matrix debonding (sliding) is activated resulting in a decrease in the nanocomposite's stiffness. Note that not all the SWNT fibers are expected to fail simultaneously; since the orientation of SWNT in the polymer is random, those tubes that have a $\pm 45^\circ$ orientation with respect to the loading direction tend to fail first because the buildup of shear stress for these tubes is the greatest.⁵ As the strain level is increased, more and more of the SWNT interfaces begin to fail resulting in a progressive reduction in the storage modulus as shown in Figure 2a. As frictional sliding at the tube-polymer interfaces is activated, we expect an increase in the loss modulus (damping) of the nanocomposite. This is clearly seen in Figure 2b, which shows that the decrease in storage modulus of the nanocomposite

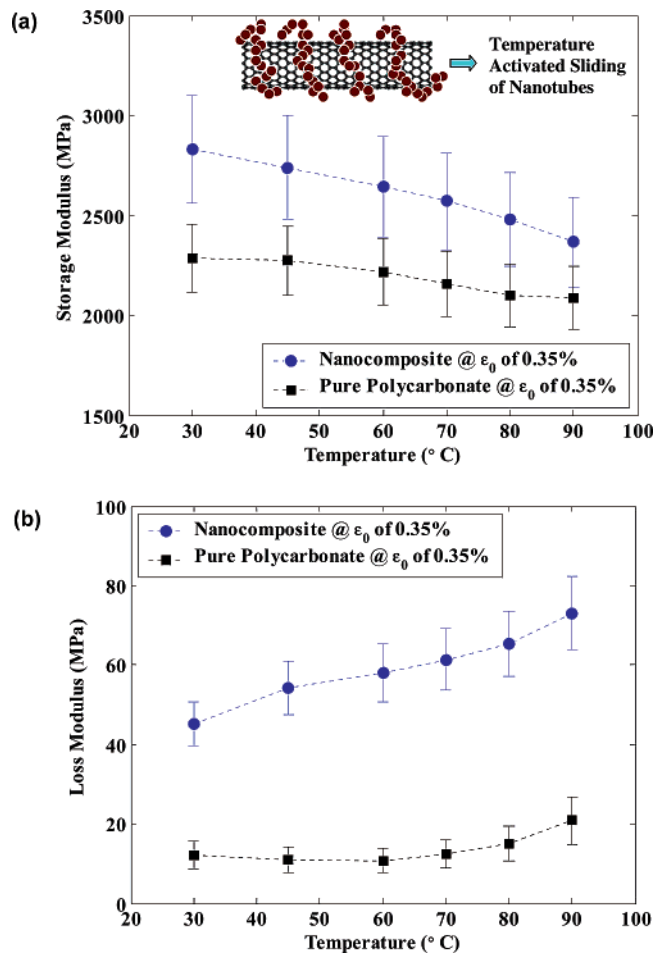


Figure 3. Performance of the pure polycarbonate and the nanocomposite samples above room temperature. (a) Results for storage modulus as a function of test temperature for constant strain amplitude (0.35%). Tests are performed at a frequency of 1 Hz. The weight fraction of the oxidized SWNT in the composite is 1.5%. The storage modulus of the nanocomposite decreases at a faster rate compared to the pure polycarbonate, which indicates that proximity to the α -transition temperature of polycarbonate helps to facilitate interfacial slip at the nanotube-polymer interfaces within the composite. This temperature activated sliding of the nanotubes is illustrated schematically in the inset. (b) Results for loss modulus as a function of test temperature at constant strain amplitude (0.35%). The nanocomposite sample shows substantially improved damping performance compared to the pure polycarbonate, which confirms that raising the temperature promotes interfacial slippage in nanotube-polymer systems.

is mirrored by a corresponding increase in loss modulus. Beyond about 1.2% strain amplitude, the loss modulus of the nanocomposite plateaus (or levels off) at about 70 MPa and is no longer very sensitive to strain. This is because interfacial slip has now been fully activated for a majority of nanotubes within the composite and further increase in strain does not serve to promote interfacial slippage. While the damping behavior of the nanocomposite displays strong amplitude dependence, the pure polycarbonate sample shows strain-independent loss modulus behavior (~ 12 MPa) over the entire strain range. This is to be expected since the polycarbonate chains are highly cross-linked at room temperature. Figure 2 also shows the effect of the test frequency on the storage and loss modulus. Clearly in the 1–10 Hz

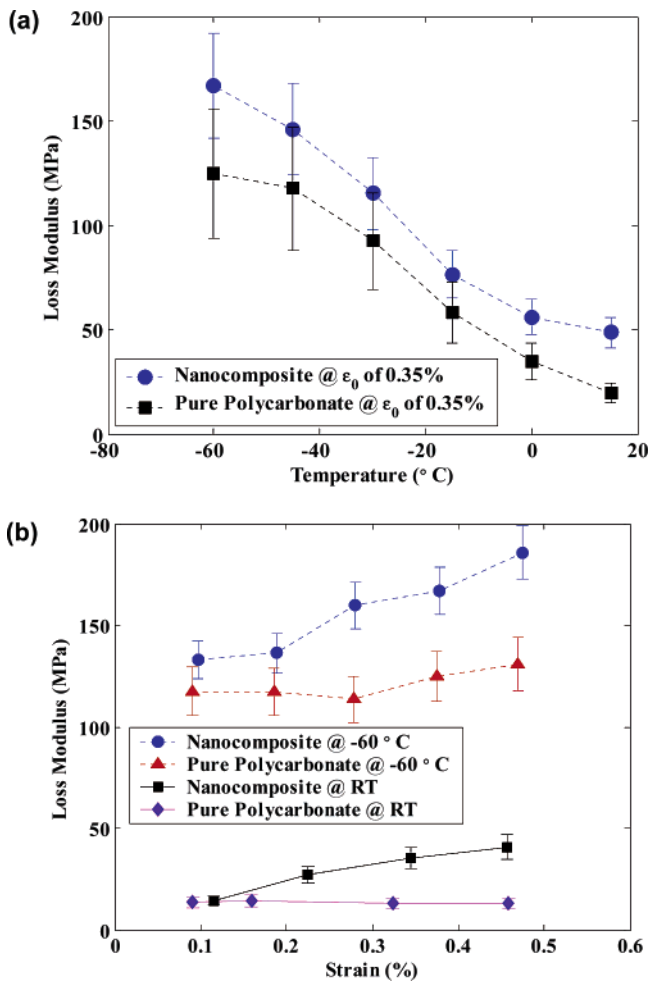


Figure 4. Performance of the pure polycarbonate and the nanocomposite samples below room temperature. (a) Results for loss moduli as a function of test temperature at a strain amplitude of 0.35%. The test frequency is kept constant at 1 Hz. The weight fraction of the oxidized SWNT in this composite is 1.5%. Close to the β transition temperature of polycarbonate (~ -60 °C), significant enhancement in damping behavior is observed for both samples due to increased mobility of the side chains in the polycarbonate. However the relative difference in loss modulus of the nanocomposite and the pure polycarbonate sample is not significantly affected by the β -relaxation of the polymer. (b) Results for loss modulus as a function of strain (0.1–0.45%) at room temperature and -60 °C. The nanocomposite sample shows similar sensitivity to strain amplitude at both temperatures, while the pure polymer displays strain independent response. This confirms that side chain mobility of the host polymer matrix has a relatively small impact on promoting interfacial slip at the nanotube–matrix junctions.

frequency range, the test frequency has a small influence on the viscoelastic properties of both the nanocomposite and the pure polymer samples.

Having characterized the room-temperature response, we proceeded to study the effect of temperature (Figure 3) on the viscoelastic properties of the nanocomposite and baseline polycarbonate samples. It is well established that polymers undergo relaxation processes (associated with various modes of molecular motions) as the temperature is varied. Among the typical relaxation processes^{11,12} of amorphous polymers, α -relaxation has the characteristics of a glass transition (i.e., enhanced mobility of polymer backbones), while the β -

relaxation process involves a local relaxation (i.e., motion of side groups attached to the polymer backbone). To study the effect of temperature, we raised the test temperature (using an MTS 651.05E environmental chamber) from room temperature to 90 °C in steps of 15 °C. Each temperature test was conducted at a fixed uniaxial strain amplitude of 0.35%. Figure 3a indicates that as the temperature is raised the storage modulus of the nanocomposite shows a marked decrease from ~ 2800 MPa at 30 °C to ~ 2500 MPa at 90 °C. Similarly the nanocomposite’s loss modulus (Figure 3b) increases with temperature from ~ 40 MPa at 30 °C to ~ 75 MPa at 90 °C. It is interesting to note that the nanocomposite’s storage modulus (for 0.35% strain amplitude) at 90 °C is similar to its room temperature storage modulus at 1.2% strain amplitude. Similarly the nanocomposite’s loss modulus (for 0.35% strain amplitude) at 90 °C is very close to its room-temperature loss modulus at 1.2% strain. At room temperature, 1.2% strain (see Figure 2) corresponds to a level of strain where interfacial slip has been activated for a majority of the nanotubes within the composite. Therefore the fact that the storage and loss modulus of the nanocomposite at 90 °C and 0.35% strain is similar to that at room temperature and 1.2% strain suggests that increasing temperature also serves to activate interfacial slip, just as increasing the strain amplitude (Figure 2) was shown to promote interfacial slippage. At elevated temperatures, as the glass transition temperature of the polymer ($T_g \sim 145$ °C for polycarbonate) is approached, the mobility of the polymer chain backbones is enhanced. This can weaken the mechanical interlocking between the nanotubes and the host structure matrix making it relatively easier to activate interfacial slip at a lower strain level. Another contributing factor could be the mismatch in the thermal expansion coefficient of the SWNTs and the host matrix material, which gives rise to a radial compressive⁸ stress at the tube–polymer interface. As the temperature is increased, this radial compressive stress is relieved⁸ thereby weakening tube–matrix adhesion and facilitating the activation of interfacial slip.

If our hypothesis that elevated temperatures facilitate the activation of interfacial slip is correct, then the sensitivity of the loss modulus to strain amplitude at elevated temperatures should be lower than that at room temperature. This follows from the fact that at elevated temperatures relatively fewer tube–matrix contacts are still intact and increasing the strain will have smaller influence under these conditions. To test this hypothesis, we varied the applied strain amplitude from 0.2% to 0.7% at a temperature of 60 °C and compared the measured loss modulus to the room temperature (25 °C) results shown in Figure 2. At room temperature the loss modulus increases by 155% from 22.5 to 58.0 MPa as the strain level is raised from 0.2% to 0.7%. At 60 °C, we observed only a 55% increase in loss modulus from about 38.35 to 59.63 MPa over the same strain range. These results support our hypothesis that elevated temperatures facilitate the activation of interfacial slip in carbon nanotube polymer composites.

We also measured the damping responses of the nanocomposites and pure polycarbonate samples below room

temperature. Figure 4a compares the data for loss moduli of the nanocomposite and pure polycarbonate as a function of temperature in the 20 to -60 °C range. As the β -transition temperature of polycarbonate (~ -60 °C) is approached, a significant enhancement in the damping behavior is observed for both the pure polycarbonate and the nanocomposite samples due to increased mobility of the side chains in the polycarbonate. However the relative difference in loss modulus of the nanocomposite and the baseline polycarbonate sample is not significantly affected by the β -relaxation of the polymer. This indicates that the increase in the energy dissipation associated with the β -relaxation effect of the polymer side chains is identical for both the nanocomposite and the pure polycarbonate system. Figure 4b compares the effect of strain amplitude on the pure polycarbonate and nanocomposite samples at room temperature and at -60 °C. At both temperatures, the nanocomposite sample shows very similar sensitivity to the strain amplitude. This confirms the observation of Figure 4a that side chain mobility of the host polymer matrix has a relatively small impact on promoting interfacial slip at the nanotube-matrix junctions.

This work represents the first study in the literature where the effect of temperature on the interfacial friction damping properties of carbon nanotube polymer composites has been characterized. We show that the damping properties of carbon nanotube composites are enhanced as the operating temperatures are increased. At elevated temperatures, interfacial nanotube-matrix slip can be activated at lower strain levels, thereby maximizing the energy dissipation capability of the system. These results suggest the strong potential of nano-

composites as high-temperature damping materials for vibration and acoustic suppression in a variety of aeronautical and space vehicles, satellites, gas turbines, microengines, and MEMS-based inertial sensors used in missiles and weapon platforms.

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