

Fabrication of Copolymer-Grafted Multiwalled Carbon Nanotube Composite Thermoplastic Elastomers Filled with Unmodified MWCNTs as Additional Nanofillers To Significantly Improve Both Electrical Conductivity and Mechanical Properties

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S Supporting Information

ABSTRACT: Nanostructured materials have attracted tremendous attention in past decades owning to their wide range of potential applications in many areas. In this study, novel conductive composite thermoplastic elastomers (CTPEs) were fabricated by using a copolymer-grafted multiwalled carbon nanotube (MWCNT) composite thermoplastic elastomer filled with varied amounts of unmodified MWCNTs as additional nanofillers. Rheological measurements and electrical conductivity tests were performed to investigate the viscoelasticity and electrical percolation behavior of these CTPEs, respectively. The incorporation of unmodified MWCNTs can significantly increase the electrical conductivity of these CTPEs, and the electrical conductivity percolation threshold was determined to be 0.34 wt %. The macroscopic mechanical properties of these CTPEs can be conveniently adjusted by the content of unmodified MWCNTs; for example, the strain-hardening behavior can be significantly enhanced with the incorporation of unmodified MWCNTs. This design concept can be generalized to other conductive composite elastomeric systems.

INTRODUCTION

Thermoplastic elastomer (TPE) is an important class of engineering elastomers that can be stretched to a high degree of deformation without rupture under stress, and can recover to their initial state after the stress is removed due to their high entropy elasticity.¹ TPEs have been used in many applications, including packing materials, automotive parts, artificial muscles, and medical devices. $^{2-6}$ To meet the demands of various critical applications, nanosized fillers, such as silica,^{7,8} carbon black,^{9,101} graphene oxide,^{11,12} and carbon nanotubes (CNTs),^{13,14} have been used to prepare elastomeric materials with high performances. Among them CNTs have received substantial attention because they can impart unique electrical and mechanical properties to a polymer matrix at low volume fractions.¹⁵ A variety of strategies involving CNTs and elastomers have been applied for the preparation of conductive composite elastomers. Shin et al. used aligned CNT forests to prepare composite elastomers with highly elastic and electrically conductive properties.¹⁶ Chun et al. fabricated highly conductive, printable, and stretchable composite films by using micrometer-sized silver flakes and CNTs decorated with self-assembled silver nanoparticles.¹⁷ The combination of rigid CNTs and elastic polymers makes the creation of highly stretchable conductive elastomers, which can be applied in electronics,¹⁸ actuators,¹⁹ sensors,²⁰ and loudspeakers.²¹

In all the studies a great challenge is making an efficient dispersion of CNTs into TPEs. A lot of methods have been used to improve the CNT dispersion, including solution blending,^{22,23} coagulation,^{24,25} melt blending,²⁶ oxidation,^{27,28} and covalent functionalization.²⁹ Covalently functionalized

CNTs have been demonstrated to be particularly useful nanofillers for reinforcement, exhibiting excellent stress transfer between filled CNTs and polymer matrix. Our group recently demonstrated that the incorporation of semirigid cellulose chains or stiff nanoobjects as hard domains into the elastomeric polymer matrixes via a grafting strategy could generate composite thermoplastic elastomers (CTPEs) with significantly enhanced mechanical properties.^{30–33} However, these CTPEs demonstrated poor electrical conductivity due to insulation of CNTs by grafted polymer brushes on their surfaces.^{34,35} We further consider that the electrical conductivity of these CTPEs could be significantly enhanced by incorporating appropriate amounts of unmodified CNTs. Herein we have fabricated conductive CTPEs by using a copolymer-grafted multiwalled carbon nanotube (MWCNT) composite thermoplastic elastomer, MWCNT-g-poly(*n*-butyl acrylate-co-methyl methacrylate) as the matrix and unmodified MWCNTs as additional nanofillers. To the best of our knowledge, there are no reports on such a type of copolymer-grafted MWCNT/MWCNT CTPEs in the literature. We consider that this approach can be generalized to other conductive composite elastomeric systems. In order to demonstrate our concept, we have fabricated a series of CTPEs filled with MWCNTs of varied contents. Rheological measurements and electrical conductivity tests were conducted to reveal the relationships between the

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Figure 1. Changes of (a) storage modulus, G', (b) loss modulus, G'', (c) loss tangent, tan δ , and (d) complex viscosity, $|\eta^*|$, as functions of angular frequency, ω , for CTPEs filled with MWCNTs of various contents as measured at 200 °C. TEM micrographs for (e) initial CTPE and (f) CTPE filled with 10.0 wt % unmodified MWCNTs.

viscoelasticity and electrical percolation behavior and the microstructures of these conductive CTPEs, respectively. Monotonic and step cyclic tensile tests have been performed to study the mechanical properties of these CTPEs.

EXPERIMENTAL SECTION

Materials. MWCNTs with an average length of 50 μ m and average diameter of 8–15 nm were provided by the Chengdu Organic Chemistry Co., Chinese Academy of Sciences. *N*,*N*-Dimethylformamide (DMF) and methanol were purchased from the Sinopharm Chemical Reagent Co. (Shanghai, China). A copolymer-grafted multiwalled carbon nanotube composite thermoplastic elastomer (CTPE) with MWCNT mass content of 1.4 wt %, termed BA6500-MWCNT1.4, was prepared according to our previous work,³⁶ where BA6500 stood for the grafted copolymer poly(*n*-butyl acrylate-*co*-methyl methacrylate) with a fixed molar ratio of BA/MMA = 6500/3500. The counterpart linear copolymer BA6500 added with 1.4 wt % unmodified MWCNTs in polymerization was prepared in a similar way with ethyl 2-bromoisobutyrate as the initiator and unmodified MWCNTs as the fillers with no grafting.

Preparation of CTPEs Filled with Unmodified MWCNTs. Coagulation was used to prepare CTPEs filled with unmodified MWCNTs. First, CTPE was dissolved in DMF at room temperature and MWCNTs were ultrasonically dispersed in DMF for 1 h. After that, MWCNT/DMF suspension and CTPE/DMF solution in certain mass ratios were mixed and stirred for 10 h to ensure sufficient mixing. Then, the mixture was precipitated into a large amount of methanol and the precipitate was filtered and dried under vacuum at 40 °C until constant mass. CTPEs filled with unmodified MWCNTs of varied contents ranging from 0 to 10.0 wt % and BA6500 (added with 1.4 wt % unmodified MWCNTs during polymerization) filled with an additional 0.34 wt % unmodified MWCNTs were prepared by the same procedure. The as-prepared CTPEs and BA6500 went through the following processing procedure eight times to fabricate film samples: cut into pieces and vacuum hot pressed under 10 MPa at 160 °C for 3 min by stacking the pieces between two polished metal plates.²⁶

Differential Scanning Calorimetry (DSC). DSC measurements were performed on a TA Q2000 DSC (TA Instruments) under nitrogen atmosphere. The Universal Analysis 2000 software (TA Instruments) was used to analyze the obtained heat flow curves, which determined the glass transition temperature, T_{g} .



Figure 2. (a) Change of electrical conductivity, σ , with MWCNT content for CTPEs. Inset shows the log–log plot of σ versus reduced MWCNT content. The solid lines are the fitted lines according to the power law dependence of σ on the reduced MWCNT content. Schematic illustrations of dispersions of MWCNTs in initial CTPE (b) and in CTPE filled unmodified MWCNTs with content above the percolation threshold (c). The purple rods stand for the copolymer-grafted MWCNTs, and the black rods stand for unmodified MWCNTs.

Transmission Electron Microscopy (TEM). To investigate the dispersion state of MWCNTs within CTPEs, ultrathin sections of the film samples were obtained by using a Leica EM FC6 ultramicrotome at -90 °C. TEM observations were performed on a JEOL JEM-2100 microscope operated at an acceleration voltage of 200 kV.

Rheological Measurements. Rheological measurements were performed on a stress-controlled rheometer, AR2000EX (TA Instruments), equipped with parallel-plate geometry (diameter of 25 mm) under a nitrogen atmosphere at 200 °C. Oscillatory frequency sweeps from 500 to 0.05 rad/s were performed at a strain amplitude of 2%, which were shown to be within the linear viscoelastic regime.

Electrical Conductivity Tests. For the conductive property tests the film samples with volume electrical resistivity below $10^6 \Omega$ cm were measured using a four-probe method (RTS-8, Guangzhou Four Probe Technology Co.), while the film samples with volume electrical resistivity higher than $10^6 \Omega$ cm were tested using a high-resistance meter (ZC36, Shanghai Anbiao Electronics Co.).

Mechanical Property Tests. Monotonic and step cyclic tensile tests were performed at room temperature using a Suns UTM2502 universal testing machine with a 100 N load cell. The crosshead speed of 10 mm/min and a constant strain rate of 0.02 s⁻¹ were chosen to perform the monotonic and cyclic tensile tests at 25 °C, respectively. The detailed experimental descriptions can be found in our previous work.³⁶

RESULTS AND DISCUSSION

Rheological Behavior of CTPEs Filled with Unmodified MWCNTs. The rheological behavior is important for understanding the structure-property relationships for polymers filled with MWCNTs from the processing and application viewpoints. The changes of storage modulus, G', and loss modulus, G'', with angular frequency, ω , for CTPEs filled with unmodified MWCNTs of various contents as measured at the temperature of 200 °C are depicted in parts a and b, respectively, of Figure 1. Evidently, the rheological properties of these CTPEs are dramatically affected by the incorporation of unmodified MWCNTs, and both *G*′ and *G*″ increase with increasing MWCNT content. The initial sample CTPE without addition of unmodified MWCNTs exhibits typical homopolymer-like terminal behavior with the scaling properties approximated by *G*′ $\approx \omega^2$ and *G*″ $\approx \omega$, indicating that the grafted chains can be fully relaxed despite an existence of 1.4 wt % MWCNTs, and the copolymer matrix.³⁶ At the intermediate frequencies between 1 and 10 rad/s, *G*′ and *G*″ show obvious reinforcement because the copolymer this time scale.^{24,37}

As the filled unmodified MWCNT contents are higher than 1.0 wt %, the terminal behavior for the CTPEs disappears and G' reaches plateau values at low frequencies, indicating a transition from the liquid-like to solid-like viscoelastic behavior.³⁸⁻⁴⁰ Absence of relaxation at low frequencies is attributed to the formation of MWCNT network that restricts the long-range motion of the grafted copolymer chains. At high frequencies the effect of MWCNTs on both moduli becomes much weaker, demonstrating that the stress relaxation is dominated by polymer relaxation. The changes in the loss tangent, tan δ , as a function of ω for the CTPEs are shown in Figure 1c. The values of tan δ evidently decrease with increasing frequency when the filled unmodified MWCNT contents are lower than 1.0 wt %, indicating a typical viscoelastic property. However, tan δ becomes independent of frequency at low frequencies when the filled MWCNT content is raised above 1.0 wt %. The changes in the complex shear viscosity, $|\eta^*|$, as a function of ω for these CTPEs are shown in Figure 1d. The complex viscosity values increase with increasing MWCNT content for these CTPEs, especially at low frequencies. It can be found that CTPEs with MWCNT contents less than 1.0 wt % show the Newtonian plateaus at low



Figure 3. (a) Monotonic nominal stress-strain curves for CTPEs filled with unmodified MWCNTs of various contents. (b) Changes of stress at break and strain at break with MWCNT content for CTPEs.

frequencies, whereas the other CTPEs with higher MWCNT contents exhibit non-Newtonian behavior, which can be explained by the significantly restricted motion of the copolymer chains due to the formation of MWCNT network.^{24,37} Parts e and f, respectively, of Figure 1 show TEM micrographs for the initial CTPE and CTPE filled with 10.0 wt % unmodified MWCNTs. It can be seen that the copolymer-grafted MWCNTs can be dispersed as individual discrete nanotubes in CTPE without aggregation or network formation (Figure 1e), whereas for the sample CTPE filled with 10.0 wt % MWCNTs, the filled MWCNTs are interconnected (Figure 1f), indicating the formation of MWCNT network.

Electrical Conductivities of CTPEs Filled with Unmodified MWCNTs. The electrical conductivities of the CTPEs strongly depend on the filled MWCNT content. Figure 2a shows the change of electrical conductivity, σ , with MWCNT content for the CTPEs, indicating an obvious percolation behavior. A power law relation can be used to determine the percolation threshold for electrical conductivity:⁴¹

$$\sigma \propto (m - m_{c,\sigma})^{\rho_{c,\sigma}} \tag{1}$$

where σ is electrical conductivity, *m* is MWCNT mass content, $m_{c\sigma}$ is the percolation threshold of electrical conductivity, and $\beta_{c,\sigma}$ is a critical exponent, which depends on the dimensionality of the conductive network. The percolation threshold is related to the dispersion of MWCNTs, and a conductive MWCNT network will form when the MWCNT content reaches the conductive threshold. As displayed in Figure 2a, the best fit of electrical conductivity data with eq 1 yields a percolation threshold, $m_{c\sigma}$ of 0.34 wt %. The critical exponent value extracted from the fitting is 5.6, which is larger than the theoretical value for the three-dimensional network. Such a high exponent value can be ascribed to a tunneling percolation network, in which broad distributions of the tunneling resistance and interparticle distance exist.⁴² Electrical properties of the CTPEs are sensitive to the interconnectivity of MWCNTs in the CTPE matrix, and the electron hopping or tunneling mechanisms require nanotube-tube distance to be less than 5 nm to reach the electrical conductivity percolation threshold.⁴³ It is well accepted that introducing an electrical network into elastomer matrixes can fabricate stretchable conductive composites with high performances. The conductivity of a semiconductor is in the range 10^{-4} –10 S/cm.⁴ Note that the electrical conductivity of the CTPE with 10.0 wt % MWCNT content reaches 1.56 S/cm. Thus, these CTPEs can be used as semiconductors. It should be noticed that the

electrical conductivity of the initial CTPE is only 9.2×10^{-15} S/ cm, indicating a poor electronic conductivity. It is interesting to clarify the role that the copolymer-grafted MWCNTs play in these CTPEs. It is widely accepted that chemical functionalization introduces defect sites and disrupts the extended π conjugation of nanotubes and thereby reduces electrical conductivity of isolated nanotubes. Hayashida et al. prepared poly(cyclohexyl methacrylate)-grafted multiwalled carbon nanotubes by surface-initiated atom transfer radical polymerization (ATRP) and found that the sample had ultrahigh electrical resistance,³⁴ which is in accordance with our result in this study. However, even though the electrical conductivity of the initial CTPE was much poorer as schematically illustrated in Figure 2b, these CTPEs become conductive by incorporating appropriate amounts of unmodified MWCNTs through the formation of MWCNT network as indicated in Figure 2c. Note that the homogeneously dispersed copolymer-grafted MWCNTs might assist the fine dispersion of unmodified MWCNTs into the initial CTPE, which is important for approaching the high electrical conductivities for the CTPEs. To confirm this statement, additional 0.34 wt % MWCNTs were incorporated into the initial CTPE and its counterpart linear copolymer BA6500 added with 1.4 wt % MWCNTs during polymerization (grafting did not occur for this sample), respectively. The electrical conductivities for the prepared CTPE and BA6500 filled with additional 0.34 wt % unmodified MWCNTs (a total 1.74 wt % MWCNTs) were 1.8×10^{-12} and 6.2×10^{-13} S/cm, respectively. This comparison indicates that the unmodified MWCNTs can be dispersed homogeneously in the CTPE matrix by our approach. Park et al. have pointed out that the filler-elastomer interactions are crucial for the fine dispersion of fillers in the rubbery matrix. For example, through chemically modifying the carbon black surfaces the interfacial adhesion between carbon black and rubber in a composite system can be enhanced.^{45,46} Costa et al. have fabricated a series of thermoplastic elastomers of styrene-butadienestyrene (SBS) copolymers filled with CNTs, and they find that the mechanical and electrical properties of these elastomeric composites are strongly related to the used elastomer matrix architecture and the content of CNTs.47-52 In our study, use of the copolymer-grafted MWCNTs (low electrically conductive CTPEs) filled with additional unmodified MWCNTs to prepare high electrically conductive CTPEs represents a unique approach.

Mechanical Properties of CTPEs Filled with Unmodified MWCNTs. The mechanical properties of the CTPEs were investigated by means of monotonic and step cyclic tensile tests. Figure 3a shows the monotonic nominal stress-strain curves for the CTPEs filled with unmodified MWCNTs of various contents. These CTPEs exhibit typical elastomeric behavior with a large elastic deformation up to a strain of 605%. The key parameters of the mechanical properties are listed in Table 1. The tensile stress at the same strain of the CTPEs

Table 1. Mechanical Properties of CTPEs Filled with Unmodified MWCNTs

MWCNT content (wt %)	T ^a (°C)	stress at break ^b (MPa)	strain at break ^b (%)	av ER ^c (%)
0	13	5.4 ± 0.3	605 ± 30	94
0.25	13	5.8 ± 0.4	591 ± 26	93
0.50	14	6.1 ± 0.3	570 ± 27	92
1.0	14	6.5 ± 0.5	530 ± 23	92
2.0	14	7.2 ± 0.6	475 ± 21	91
4.0	14	8.1 ± 0.5	398 ± 18	90
6.0	15	9.3 ± 0.6	330 ± 17	81
8.0	15	11.2 ± 0.8	244 ± 14	73
10.0	16	13.3 ± 0.7	178 ± 15	65
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^aMeasured by DSC. ^bDetermined from monotonic nominal stressstrain curves. ^cDetermined from step cyclic nominal stress-strain curves.

increases as the MWCNT content increases, demonstrating that the tensile modulus can be enhanced efficiently by addition of unmodified MWCNTs. To illustrate the relationship between the mechanical properties and the content of added unmodified MWCNTs, the changes of stress at break and strain at break with MWCNT content are displayed in Figure 3b. Note that the stress at break increases linearly from 5.4 to 13.3 MPa while the strain at break decreases linearly from 605 to 178% when the MWCNT content increases from 0 to 10.0 wt

%, indicating that the mechanical properties of the CTPEs can be tuned systematically by the amount of added unmodified MWCNTs to meet the demands of practical applications. For thermoplastic elastomers, the glass transition temperature, T_{o} , is a key parameter that determines the applied mechanical properties. The DSC heat flow curves for the CTPEs filled with unmodified MWCNTs are shown in Figure S1. It can be found that the $T_{\rm g}$ value increases from 13 to 16 $^{\circ}{\rm C}$ as the MWCNT content increases from 0 to 10.0 wt %, which can be attributed to the introduction of MWCNT network that restrains the mobility of the grafted copolymer chains. The monotonic nominal stress-strain curves for the CTPE filled with additional 0.34 wt % unmodified MWCNTs and its counterpart linear copolymer BA6500 filled with a total 1.74 wt % unmodified MWCNTs (added with 1.4 wt % unmodified MWCNTs during polymerization and then filled with additional 0.34 wt % unmodified MWCNTs in mixing) are displayed in Figure S2. It can be found that the CTPE filled with additional 0.34 wt % MWCNTs exhibits obviously enhanced mechanical properties compared with its counterpart BA6500 filled with a total 1.74 wt % unmodified MWCNTs, which is in accordance with the electrical conductivity results, demonstrating again that the copolymer-grafted MWCNTs indeed assist the fine dispersion of unmodified MWCNTs into the elastomeric matrix.

Typical nominal stress—strain curves for the CTPEs filled with unmodified MWCNTs of varying contents during step cyclic tensile deformation series are shown in Figure 4a—c and Figure S3. It can be found that in a given cycle the ongoing loading curve does not trace the previous loading curve, and the residual strains at zero stress are progressively larger and larger. Compared with the preceding loading cycle, the second or later



Figure 4. Nominal stress-strain curves during step cyclic tensile deformation measured at 25 $^{\circ}$ C with a constant strain rate of 0.02 s⁻¹ for CTPEs with filled MWCNT contents of (a) 0, (b) 4.0, and (c) 8.0 wt %. (d) Evolutions of elastic recovery with maximum strain during step cyclic tensile tests for CTPEs. The dashed line in (d) points to the elastic recovery value of 90%.



Figure 5. (a) Illustration of the Gaussian model proposed by Haward and Thackray. Gaussian plots of true stress, σ_{true} , as a functions of $\lambda^2 - 1/\lambda$ for CTPEs filled with MWCNTs of (b) 0, (c) 4.0 and (d) 8.0 wt % during loading in the step cyclic tensile deformation series. Plots of (e) strain-hardening modulus (G_p) and (f) energy dissipation rate versus maximum strain in each cycle for CTPEs.

loading cycles show more rubbery character with lower initial moduli. This stress-softening effect known as the Mullins effect has been widely investigated in nanostructured elastomers.^{53,54} The elastic recovery (ER) of the CTPEs can be estimated from the nominal stress versus nominal strain curves as ER = $100\%(\varepsilon_{\max} - \varepsilon_p(0,\varepsilon_{\max}))/\varepsilon_{\max}$, where ε_{\max} and $\varepsilon_p(0,\varepsilon_{\max})$ are the maximum strain and the strain at zero stress in the cycle after the maximum strain, ε_{max} , respectively. Figure 4d shows the changes of elastic recovery with maximum strain in each cycle, revealing different elastic recovery features in the CTPEs with varied MWCNT contents. The average ER value decreases when more MWCNTs are incorporated into the CTPEs, revealing an increase of the plastic deformation proportion during deformation. Nevertheless, when the MWCNT contents are less than 4.0 wt %, the CTPEs possess sufficient elastic recovery and the average ER values can be above 90% during loading-unloading cycles.

The Gaussian model proposed by Haward and Thackray^{55,56} as displayed in Figure 5a was used for the purpose of investigating the mechanical properties of the CTPEs more clearly. This model combines a Hookean spring with an Eyring dashpot and a rubbery spring in parallel to investigate the

mechanical properties of thermoplastics at large strains. The rubbery spring in our case corresponds to the soft PBA phase domains, while the Hookean spring and the dashpot correspond to the dispersed hard phase domains (rigid MMA segmental domains and MWCNTs) and chain slips, respectively. The true stress, σ_{true} , can be represented by eq 2 according to the Gaussian model:

$$\sigma_{\rm true} = \lambda \sigma_{\rm eng} = G_{\rm p} (\lambda^2 - 1/\lambda) \tag{2}$$

where σ_{eng} is defined as engineering stress, λ represents the draw ratio, and G_p can be called the strain-hardening modulus. The values of G_p (slopes at high $\lambda^2 - 1/\lambda$) during loading in the step cyclic tensile deformations can be obtained from the Gaussian plots as shown in Figure 5b–d and Figure S4. Clearly, the strain-hardening behavior becomes more obvious after several loading and unloading cycles. To reveal the role that MWCNTs play, the changes of G_p value with the maximum strain in each cycle are plotted in Figure 5e. It is noticed that at the same strain the value of G_p increases as the MWCNT content increases, indicating that the strain-hardening behavior is strongly related to the incorporation of MWCNTs. When the



Figure 6. Changes of true plastic ($\varepsilon_{H,p}$) and elastic ($\varepsilon_{H,e}$) strains as functions of true maximal strain (ε_{Hmax}) for CTPEs filled with MWCNTs of (a) 0, (b) 2.0, (c) 4.0, (d) 6.0, (e) 8.0, and (f) 10.0 wt % during step cyclic tensile deformation.

MWCNT contents in the CTPEs are no more than 2.0 wt %, the values of G_p are small and increase slightly as the strain increases. However, when more MWCNTs are introduced, G_p increases rather rapidly at the low strains and continues to increase until saturation as the strain further increases. At the maximum strain of 150%, the value of G_p increases from 0.7 to 10.2 MPa when the MWCNT content increases from 0 to 10.0 wt %. Figure 5f shows the changes of energy dissipation rate with maximum strain in each cycle for the CTPEs filled with different contents of unmodified MWCNTs. It can be found that the energy dissipation rate increases as the MWCNT content increases at the same maximum strain. The above result can be attributed to the presence of additional unmodified MWCNTs as physical cross-linking points. The increase in stress for large strains in combination with the dissipative nature of the stress in the strain-hardening regime indicates that there is an increase in energy dissipation rate when more unmodified MWCNTs are incorporated, which means that more energy per unit of strain is needed for further deformation. Thus, the strain-hardening behavior in the CTPEs can be significantly enhanced by the incorporation of additional MWCNTs.

Filled elastomers often exhibit enhanced mechanical properties as compared with the nonreinforced counterparts. The study on the unique nonlinear and plastic behaviors of filled elastomers is interesting, opening the way for the prediction of macroscopic performances of filled elastomers according to the fillers and dispersion state.⁵⁷⁻⁶⁰ According to the method proposed by Strobl and co-workers,^{61,62} the true elastic strain $(\varepsilon_{\rm H,e})$ and true plastic strain $(\varepsilon_{\rm H,p})$ during step cyclic tensile deformation series can be extracted from the true stress-true strain curves. Changes of true elastic strain and true plastic strain as functions of the maximal true strain for the CTPEs filled with varied amounts of unmodified MWCNTs during cyclic tensile tests are shown in Figure 6. Both the true plastic strain and true elastic strain are low at small deformations and increase as the maximal true strain increases. When the MWCNT contents are no more than 4.0 wt %, the true elastic strain values are higher than the true plastic strain values in the whole strain range, demonstrating that the tensile deformation is mainly dominated by elastic deformation. For the CTPE filled with 4.0 wt % MWCNTs, the true elastic strain grows more rapidly than true plastic strain at small deformations, while at higher deformations, the true plastic strain grows faster than true elastic strain, which means that the plastic

deformation begins to dominate the deformation with further loading. When more MWCNTs are introduced, the true plastic strains are higher than the true elastic strain during tensile deformation. Therefore, it can be concluded that the plastic deformation is strongly related to the filled MWCNT content. In general, elastomers are entropic systems with flexible segments of chains acting as springs and chemical or physical cross-links acting as knots. In the undeformed state, the flexible chain segments are in the disordered random coil conformation and the presence of knots prevents the elastomer from flowing during tensile deformation. After the release of stress, the flexible chain segments return to the disordered coil conformation, and the whole elastomer tries to recover to the initial shape in the undeformed state.⁶³ For the CTPEs, the soft amorphous chains also experience a reversible conformational transition between the coiled and the extended conformations during the loading and unloading process. When additional MWCNTs are incorporated into the elastomer matrix, the local copolymer chain flexibility and chain segmental mobility are much reduced, leading to increase of plastic deformation.

In general, the performance and appearance of composite thermoplastic elastomers are largely influenced by the type and the amount of the filled nanofillers.¹⁰ Therefore, additional unmodified MWCNTs are introduced to the CTPE with the aim of broadening its utility. It is necessary to illustrate the roles that the copolymer-grafted MWCNTs and additional unmodified MWCNTs play in the CTPEs. In the initial CTPE, the copolymer-grafted MWCNTs are distributed homogeneously acting as physical cross-linking points, and the interfacial adhesion between copolymer-grafted MWCNTs and copolymer matrix is strong through chemical bonding. However, the CTPE behaves as an insulator because the copolymer-grafted MWCNTs are wrapped and isolated individually at a long distance by the copolymer chains, whereas the added unmodified MWCNTs can serve as bridges of neighboring individual copolymer-grafted MWCNTs to significantly enhance the mechanical and electrical conductivity properties. The incorporation of additional unmodified MWCNTs promotes the formation of MWCNT network in the CTPEs, leading to a lower electrical conductivity percolation threshold. By manipulating the content of incorporated unmodified MWCNTs, a broad spectrum of conductive elastomers can be accessed with desirable electrical conductivities as well as the enhanced mechanical properties.

CONCLUSIONS

In summary, we have prepared a series of conductive composite thermoplastic elastomers (CTPEs) by using a copolymergrafted multiwalled carbon nanotube composite thermoplastic elastomer (CTPE) as the matrix and unmodified MWCNTs as additional nanofillers. Both rheological and electrical conductivity properties of the CTPEs have been investigated at first. The storage modulus, G', loss modulus, G'', and complex shear viscosity, $|\eta^*|$, increase monotonically with increasing MWCNT content. The percolation threshold of electrical conductivity is determined by plotting the electrical conductivity versus MWCNT content and fitting to a power law relation, and the obtained electrical conductivity percolation threshold is 0.34 wt %. The electrical conductivity can be systematically adjusted by changing the MWCNT content. The mechanical properties of the CTPEs have been further investigated by monotonic and step cyclic tensile tests, which indicates that the incorporation of additional MWCNTs as

nanofillers can successfully enhance the tensile modulus and stiffness. The strain-hardening behavior becomes more obvious as the MWCNT content increases due to the presence of additional MWCNTs acting as physical cross-linking points. The results in this work confirm that both electrical conductivity and mechanical properties of the CTPEs can be significantly enhanced by introducing unmodified MWCNTs as nanofillers to broaden the applications of such copolymergrafted MWCNT elastomeric materials. This robust and efficient strategy can be also applied to other polymer-grafted MWCNT composite materials to improve the electrical conductivity and mechanical performances.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.5b03599.

Figure S1, DSC heat flow curves for samples; Figure S2, monotonic nominal stress—strain curves for CTPE filled with additional 0.34 wt % MWCNTs and its counterpart linear copolymer BA6500 filled with a total 1.74 wt % MWCNTs; Figures S3 and S4, nominal stress—strain curves and corresponding Gaussian plots for CTPEs filled with different amounts of unmodified MWCNTs (PDF)

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Notes

The authors declare no competing financial interest.

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