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Enhancement of Electrical Conductivity by Changing phase Morphology for Composites Consisting of Polylactide and Poly(ε-caprolactone) Filled with Acid-Oxidized Multiwalled Carbon Nanotubes

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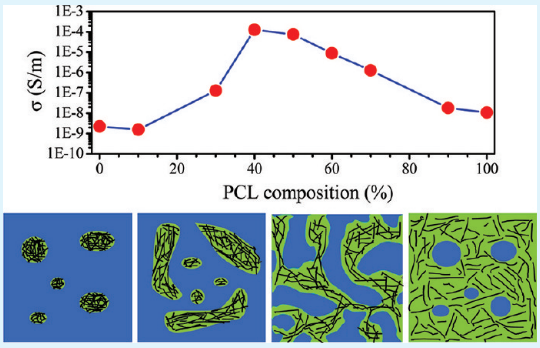
Supporting Information



ABSTRACT: Composites consisting of polylactide (PLA) and poly(ε-caprolactone) (PCL) filled with acid-oxidized multiwalled carbon nanotubes (A-MWCNTs) were prepared through melt compounding. Phase morphologies of PLA/PCL/A-MWCNT composites with different contents of filled A-MWCNTs and PCL compositions were mainly observed by scanning electron microscope. The results show that A-MWCNTs are selectively dispersed in the PCL phase, regardingless of PCL phase domain sizes. For PLA/PCL/A-MWCNT composites with fixed PLA/PCL ratio of 95/5, the dispersed PCL phase domain sizes in the PLA matrix decrease even though a small content of A-MWCNTs is added, compared with PLA/PCL blend with the same composition, indicating that A-MWCNTs effectively prevent from coalescence of the dispersed PCL phase domains. With filling of 1.0 wt % A-MWCNTs, an interesting change of electrical conductivity for PLA/PCL/A-MWCNT composites is observed, in which the maximum conductivity is observed for PLA/PCL/A-MWCNT composite with PLA/PCL ratio of 60/40. The result is well-explained by the formed cocontinuous phase morphology and effective A-MWCNT content.

KEYWORDS: *polylactide, multiwalled carbon nanotubes, composites, phase behavior, electrical conductivity*

1. INTRODUCTION

Biodegradable polymers, such as polylactide (PLA) and poly(ε-caprolactone) (PCL), have generated a great deal of interest as ones of the most innovative materials being developed for a wide range of applications because of their thermoplastic, biodegradable, and biocompatible properties.[1,2] Blending of two or more polymer components is a novel method for producing balanced properties for specific end uses. However, most polymers are thermodynamically immiscible and their blends produce immiscible phase domains with sharp interfaces, because of their unfavorable interactions and high molecular masses. The final properties of blends are strongly influenced by the interface and the size scales of the minor phase, which are determined by the processing conditions and morphological development.

It is thought that polymer composites with polymer blends as the matrix may be new types of high performance composite materials, which combines the advantages of polymer blends and the merits of polymer composites. Addition of inorganic fillers to an immiscible polymer blend provides an alternative way to modify the interfacial properties, such as addition of carbon black (CB), organoclay or carbon nanotubes.[3−9] Gubbels et al. showed a selective location of CB at the interface between PE and PS phases that form a cocontinuous blend, dramatically reducing the amount of filled CB for percolation.[10−12] Wang et al. investigated the PS/PP/organoclay system, in which the PS domain sizes were greatly reduced upon addition of organoclay.[13] They attributed this result to the fact that the two immiscible polymer components can coexist within the intercalated clay platelets. The coexisting polymer chains play the role of a compatibilizer, like a block copolymer, for the PS/PP/organoclay system. Hong et al. prepared PBT/PE/clay composites and found that clay platelets were selectively dispersed in PBT phase.[14] Li et al. tried to determine how multiwalled carbon nanotubes (MWCNTs) acted as a compatibilizer for the PVDF/PA/MWCNT system.[15] Their

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Table 1. Compositions of PLA/PCL/A-MWCNT Composites and PLA/PCL Blends

sample	composition (wt%)							
PLA/PCL	95/5	90/10	70/30	60/40	50/50	40/60	30/70	10/90
PLA/PCL/A-MWCNT	100/0/0.5	0/100/0.5	95/5/0	95/5/0.5	95/5/1	95/5/2	95/5/4	95/5/6
PLA/PCL/A-MWCNT	95/5/1	90/10/1	70/30/1	64/40/1	50/50/1	40/60/1	30/70/1	10/90/1

results indicated that MWCNTs were exclusively located in PA6 phase domains and the formation of PA6 nanodomains in PVDF phase by the high-shear processing not only increased the electrical conductivity but also improved the ductility of the obtained composites. Zou et al. investigated the phase morphological changes induced by addition of some MWCNTs to the PPS/PA66 (60/40) blend, for which with increasing MWCNT content the morphology changed from a sea-island structure to a cocontinuous structure, and then changed back to a sea-island structure.[16] MWCNTs were also found to selectively disperse in PA66 phase, and its assembling determined the final morphology of PPS/PA66/MWCNT composites. Bailly et al. investigated in details on the selective dispersion and migration of carbon nanotubes in immiscible polymer blends of polyamide and ethylene−acrylate copolymer, in which both unfunctionalized and functionalized MWCNTs were added, respectively.[7−9]

Polymeric materials with a cocontinuous two-phase structure, i.e. the morphology with dual-phase continuity, are receiving increased attention and are extensively discussed in reference to the percolation theory. Percolation of MWCNTs in one continuous phase or at the interface of a cocontinuous binary polymer blend is more complex; however, it is also more attractive, because a double percolation phenomenon can provide the polymeric materials with sufficient electrical conductivity at a low MWCNT content.[3,17,18] The resulting electrical properties depend on location of the conductive fillers as well as the final morphology.

Although several studies were reported for PLA/PCL/nanofiller composites, the selected PCL composition was lower than 5 wt % for the purpose of modifying the mechanical properties.[19−21] Wu et al. investigated PLA/PCL/MWCNT composites with the fixed PLA/PCL ratio of 70/30 added with different MWCNT contents.[6,22] Few have been carried out for PLA/PCL/MWCNT composites with a wide range of PLA/PCL ratio. In this contribution, we investigate the effects of A-MWCNTs on phase morphologies and related electrical conductivities for PLA/PCL/A-MWCNT composites with various PLA/PCL ratios.

2. EXPERIMENTAL SECTION

Materials. Polylactide (trade name 4032D, NatureWorks China/Hong Kong, Shanghai, China) used in this study was commercial product with 98.7 mol % L-isomeric content in pellet form, density of 1.24 g/cm^3, mass averaged molecular mass of ca. 160 kg/mol and polydispersity of 1.67 (the latter two values were measured by using Waters 2414 GPC, Waters Corporation, USA). Poly(ε-caprolactone) (PCL) with mass-averaged molecular mass of 68 kg/mol was purchased from the Aldrich company. Pristine MWCNTs (P-MWCNTs) with diameters of 10−20 nm, average length of about 30 μm, special surface area (SSA) higher than 200 m^2/g, purity higher than 95% and ash content less than 1.5% were supplied by the ChengDu Organic Chemistry Co. Ltd., Chinese Academy of Sciences. P-MWCNTs were produced by the chemical vapor deposition method. Other reagents were purchased from the Beijing Chemical Reagents Company and were dried before use.

Preparation of A-MWCNTs and PLA/PCL/A-MWCNT Composites. P-MWCNTs were mixed with sulfuric acid (98%) and nitric acid (68%) (3:1 in volume), treated in ultrasonic bath for 1 h, and then refluxed at 60 °C for 4 h to obtain the acid-oxidized MWCNTs (A-MWCNTs). The excess acids were washed thoroughly with deionized water until the pH value was about 7.0. A-MWCNTs were dried in vacuum at 60 °C overnight and then ground to powder in an agate mortar. The carboxyl group mass percent of about 8.7 wt % for A-MWCNTs was measured by thermogravimetric analysis (Perkin-Elmer 7 TGA analyzer, PerkinElmer, Inc., USA). The sample weight was about 3 mg. The measurement was performed in flowing nitrogen atmosphere in a temperature range from 50 and 750 °C at a heating rate of 20 °C/min. Dilute solution of A-MWCNTs in chloroform was dropped on clean aluminum foils to form thin film after chloroform evaporated, and the thin film was subjected to SEM observation (SEM Hitachi S-4800, made in Japan). Length distribution of A-MWCNTs could be obtained from the SEM image. An Image Pro Plus software was applied to measure the lengths of A-MWCNTs. Since the SEM observation showed that the diameters of A-MWCNTs remained about 10−20 nm, the A-MWCNT aspect ratios of about 31−62 could be estimated. The average length of A-MWCNTs was about 615 nm.[23]

PLA was dried at 60 °C and PCL was dried at 40 °C in a vacuum for 6 h before use. PLA/PCL/A-MWCNT composites were prepared by using melt compounding method. Prior to melt mixing, PLA, PCL, and A-MWCNTs were premixed. Compounding of these compounds was carried out under nitrogen flow at 180 °C and 150 rpm by using 5 g capacity HAAKE MiniLab (Thermo Fisher Scientific Co., USA). The mixing time was 8 min. For comparison purpose, PLA/PCL blends were prepared by using the same procedure. The mass compositions of PLA/PCL/A-MWCNT composites and PLA/PCL blends are summarized in Table 1. For PLA/PCL/A-MWCNT composites, PLA and PCL components together weight 100 parts (by mass) and the A-MWCNT parts compared with 100 parts of PLA and PCL components are used to represent the A-MWCNT contents for simplicity due to the low A-MWCNT additions (for example, for 95/5/6 composition, the A-MWCNT content in the composite is 6/(95 + 5 + 6) = 5.7 wt %). For SEM observation, rheological measurements and electrical property tests, all the extruded samples were hot-pressed at 180 °C in a vacuum for 3 min.

Evaluation of Dispersion of A-MWCNTs in the Composites. Scanning electron microscope (SEM, Hitachi S-4800, made in Japan) was used to evaluate the dispersion of A-MWCNTs in the fractured surfaces of the composites. Before SEM observation, the composites were fractured in liquid nitrogen and then the fractured surfaces were sputtered with platinum.

Rheological Measurements on PLA/PCL/A-MWCNT Composites. To measure the rheological properties of PLA/PCL/A-MWCNT composites, we employed a stress-controlled rheometer (AR2000, TA Instruments, USA) with parallel-plate geometry (diameter of 25 mm). Before rheological measurements, the dried PLA/PCL/A-MWCNT composites were pressed at 180 °C in vacuum into disks with thickness of 1 mm and diameter of 25 mm using stainless steel dies. The disk-like samples were further dried at 60 °C in vacuum for 6 h before the measurements. Oscillatory frequency sweeps ranging from 0.1 to 500 rad/s with a fixed strain of 0.5% (falling in the linear viscoelasticity regime) were performed at 180 °C in nitrogen atmosphere for PLA/PCL/A-MWCNT composites. After the sample loading, an approximate 5 min equilibrium time was applied prior to each frequency sweep. Oscillatory time sweeps were preformed to ensure the dried composites did not show obvious storage modulus and viscosity changes for at least 3 h at the testing temperature.

Electrical Conductivity Tests. A Model 6517B Electrometer/High Resistance Meter (Keithley Instruments Inc., USA) was used to measure volume conductivities of the PLA/PCL/A-MWCNT composites at room temperature. The composites were compression-molded into disks of diameter of 25 mm and thickness of 1.0 mm by pressing at 180 °C. For the electrical conductivity tests the compression-molded disks were cut into bars with dimensions of 20 mm × 4 mm × 1 mm. Silver paste was coated on the left and right plane surfaces of the sample bar to ensure good contacts of the surfaces with the electrodes of the electrometer. The resistance between two silver paste marks along the specimen length direction was measured at room temperature. The volume resistivity was calculated in relation to the specimen dimensions. The measured volume resistance, R_v, was converted to volume conductivity, using the formula $\sigma = L/(R_vA)$, where A is the effective area of the specimen and L is the specimen length. Three specimens for each composite were tested with three data points taken on each specimen.

3. RESULTS AND DISCUSSION

Dispersion of A-MWCNTs in PLA and PCL Matrix. Dispersion of MWCNTs in polymer matrix is one of the most important topics for fabricating high performance polymer/MWCNT composites. A homogeneous dispersion of MWCNTs and sufficient interfacial interactions between polymer matrix and MWCNTs can effectively improve the mechanical, thermal, and electrical properties of polymer composites.[24] Dispersions of P-MWCNTs in PLA/P-MWCNT composites and A-MWCNTs in PLA/A-MWCNT and PCL/A-MWCNT composites were observed by SEM, respectively. Typical SEM micrographs (fractured surfaces) for the composites with MWCNT content of 0.5 wt % are shown in Figure 1. For the SEM micrographs the bright regions are attributed to MWCNTs due to their high electrical conductivity. It can be seen from Figure 1a the dispersion of P-MWCNTs in PLA matrix is heterogeneous with clearly seen large P-MWCNT aggregates. On the contrary, A-MWCNTs are found to be more much uniformly dispersed with no obvious aggregations at a submicrometer scale in Figure 1b for PLA/A-MWCNT composite and in Figure 1c for PCL/A-MWCNT composite. P-MWCNTs show obvious heterogeneous dispersion in the composites with much large scale MWCNT aggregates, which is not allowed for a comparison study. We note that there exists a bit of small size A-MWCNT aggregates in micrographs b and c in Figure 1. However, compared with the dispersion of P-MWCNTs in PLA matrix, the dispersion of A-MWCNTs in PLA or PCL matrix is acceptable for further studies in this work. The homogeneous dispersion of A-MWCNTs in the composites is mainly facilitated by interactions between the functional carboxyl group on A-MWCNT surfaces and PLA or PCL chains. In addition, better dispersion of A-MWCNTs in PLA or PCL matrix is also due to shortening of pristine MWCNT lengths by treatments with strong oxidizing agents and ultrasonic. Similar results were observed for A-MWCNT/PLA composites processed by melt mixing.[25,26] It is interesting to note that A-MWCNTs show relatively more homogeneous dispersion in PLA matrix than in PCL matrix, because PLA chains show more or less better affinity to A-MWCNTs than PCL chains, consistent with other studies on PLA/A-MWCNT and PCL/A-MWCNT composites.[6,27]

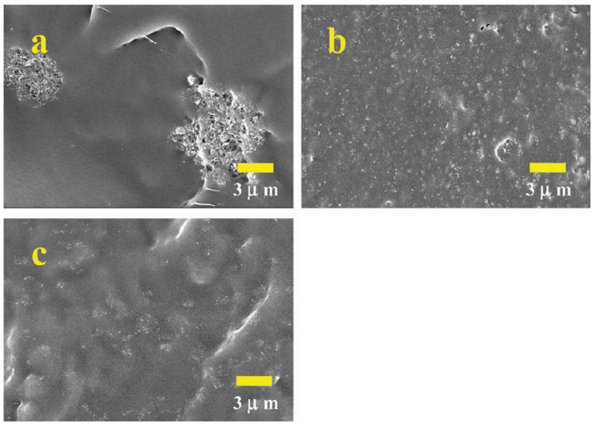

Figure 1. SEM micrographs for the composites with MWCNT content of 0.5 wt %. (a) PLA/P-MWCNT composite; (b) PLA/A-MWCNT composite; (c) PCL/A-MWCNT composite.

Selective Dispersion of A-MWCNTs in PLA/PCL/A-MWCNT Composites. Figure 2 shows SEM micrographs for PLA/PCL/A-MWCNT composites with different A-MWCNT contents. The PLA/PCL ratio in the composites is fixed at 95/5. It can be seen from Figure 2 that A-MWCNTs are preferentially located into the minor PCL phase domains. A high magnitude SEM micrograph for clarification of the A-MWCNT selective dispersion in the minor PCL phase domains can be found in the Supporting Information. Note that the fibers appearing between PLA and PCL phase domains in Figure 2a are possibly stretched out from the PLA phase during fracture due to the much higher molecular masses of PLA component. Even with addition of low content of A-MWCNTs of 0.5 wt % in the composite (corresponding to PLA/PCL/A-MWCNT composite with the composition of 95/5/0.5), the minor PCL domain sizes (averaged size of about 0.6 μm in diameter, see Figure 2b) decrease to about a half of that with no

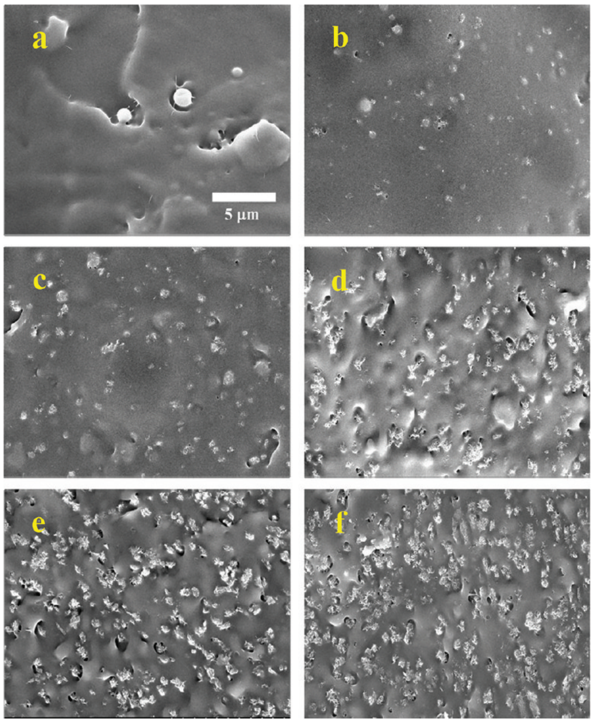

Figure 2. SEM micrographs for PLA/PCL/A-MWCNT composites with A-MWCNT content of (a) 0, (b) 0.5, (c) 1.0, (d) 2.0, (e) 4.0, and (f) 6.0 wt %. The PLA/PCL ratio in the composites is fixed at 95/5. The scale bar in a representing 5 μm is applied to all other micrographs.

adding of A-MWCNTs (averaged size of about 1.2 μm in diameter, see Figure 2a). As the A-MWCNT content increases, the domain sizes of minor PCL phase keep about invariant (averaged sizes of 0.4–0.6 μm, see Figure 2c–f; note that if the PCL phase domains are elongated, the minor axis diameters are used for the size estimate). The above result indicates that A-MWCNTs play an important role in reducing PCL domain sizes for PLA/PCL/A-MWCNT composites. The minor PCL phase and interfaces are enriched with filled A-MWCNTs. Even for the higher A-MWCNT contents, such as 6.0 wt %, A-MWCNTs are still mainly dispersed in the PCL phase domains and phase interfaces. A-MWCNTs dispersed at the phase interfaces thus blur the PCL and PLA phase domain boundaries. Another observation is that in PLA/PCL blend, PCL phase domains appear as spherical shape, whereas in PLA/PCL/A-MWCNT composites, PCL phase domains are distorted to irregular shapes because of the addition of A-MWCNTs.[14] One might argue that the decreased PCL phase domain sizes in PLA/PCL/A-MWCNT composites might be attributed to the increased viscosities of the composites. If the elasticity of composites becomes strong, phase domain sizes of the composites prepared by melt mixing could become small. For checking this possibility, the changes of complex viscosities, $|\eta^*|$, with A-MWCNT content for PLA/PCL/A-MWCNT composites are compared (see Figure 3). It is clearly seen that the difference in complex viscosities between PLA/PCL blend and PLA/PCL/A-MWCNT composite with A-MWCNT content of 1.0 wt % in the Newtonian region is not that much obvious. Therefore, the slightly increased viscosity due to addition of A-MWCNTs is not solely responsible for the decrease of PCL phase domain sizes. Instead, a barrier effect from A-MWCNTs for preventing from coalescence of the minor PCL phase domains enriched with A-MWCNTs might provide a more reasonable explanation.[5,14]

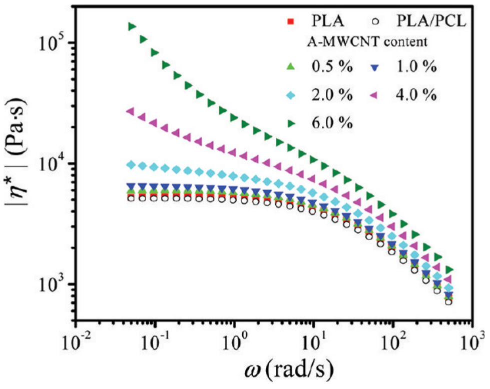

Figure 3. Changes of complex viscosity ($|\eta^*|$) with frequency for PLA/PCL/A-MWCNT composites with different A-MWCNT contents. The PLA/PCL ratio in the composites is fixed at 95/5. Rheological measurements were performed at 180 °C with a strain of 0.5%.

EFFECTS OF A-MWCNTS ON MORPHOLOGY OF PLA/PCL/A-MWCNT COMPOSITES

Morphology of PLA/PCL Blends. Figure 4 gives SEM micrographs of fractured surfaces for PLA/PCL blends with various compositions. Dispersed droplets of the minor PCL component in PLA matrix are observed for PLA/PCL 90/10 and 70/30 blends (Figure 4a, b). In a similar way, dispersed droplets of the minor PLA component in PCL matrix are observed for PLA/PCL 10/90 and 30/70 blends (Figure 4f, g). For PLA/PCL 60/40, 50/50 and 40/60 blends, the morphologies show elongational cocontinuous phase domains (Figure 4c–e). This result suggests that a phase inversion occurs for PLA/PCL blends at the PCL compositions of 30–40 wt %. The viscosity of PCL at 180 °C is far lower than that of PLA, which is indicative of a high viscosity ratio of about 23 in the Newtonian region between PLA and PCL components for the blends. Derivation from a theoretical prediction is actually in line with the argument according to which the more elastic PLA phase tends to form the matrix, similar to the results shown for the PE/PS system.[10,28] A similar phenomenon was also reported by Wu et al. in their recent work and was ascribed to higher elasticity for PLA than PCL.[29]

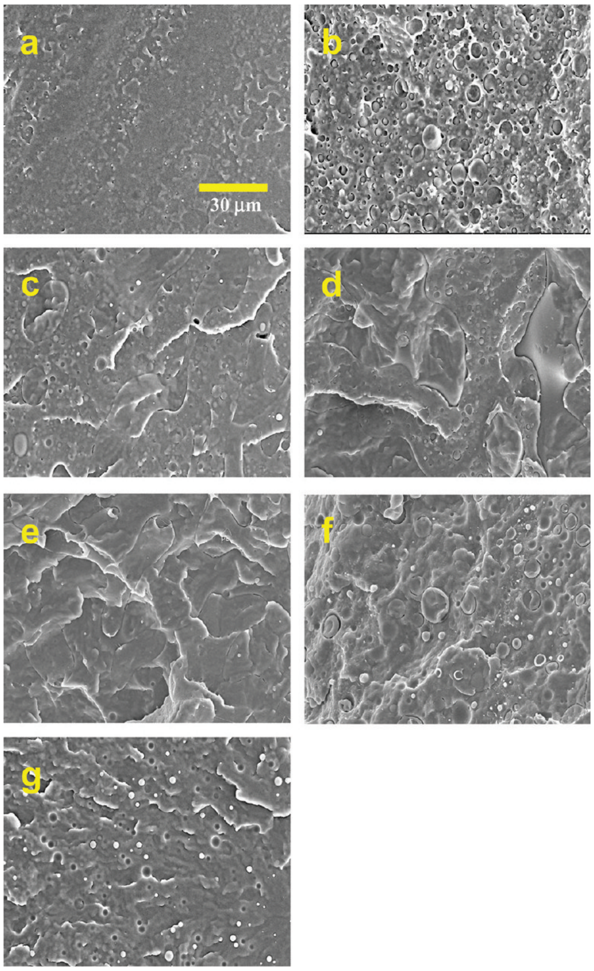

Figure 4. SEM micrographs for PLA/PCL blends with various compositions. (a) 90/10, (b) 70/30, (c) 60/40, (d) 50/50, (e) 40/60, (f) 30/70, (g) 10/90. The scale bar in a representing 30 μm is applied to all other micrographs.

Morphology of PLA/PCL/A-MWCNT Composites. Addition of A-MWCNTs plays an important role for the morphological development of PLA/PCL/A-MWCNT composites. As can be seen from Figure 5, the morphologies change from sea-island phases for PLA/PCL/A-MWCNT composite with PCL composition of 10 wt % to coexisting elongational and dispersed phases for PLA/PCL/A-MWCNT composite with PCL composition of 30 wt %, to cocontinuous phases for PLA/PCL/A-MWCNT composites with PCL compositions of 40–60 wt %, and then back to sea-island phases for PLA/PCL/

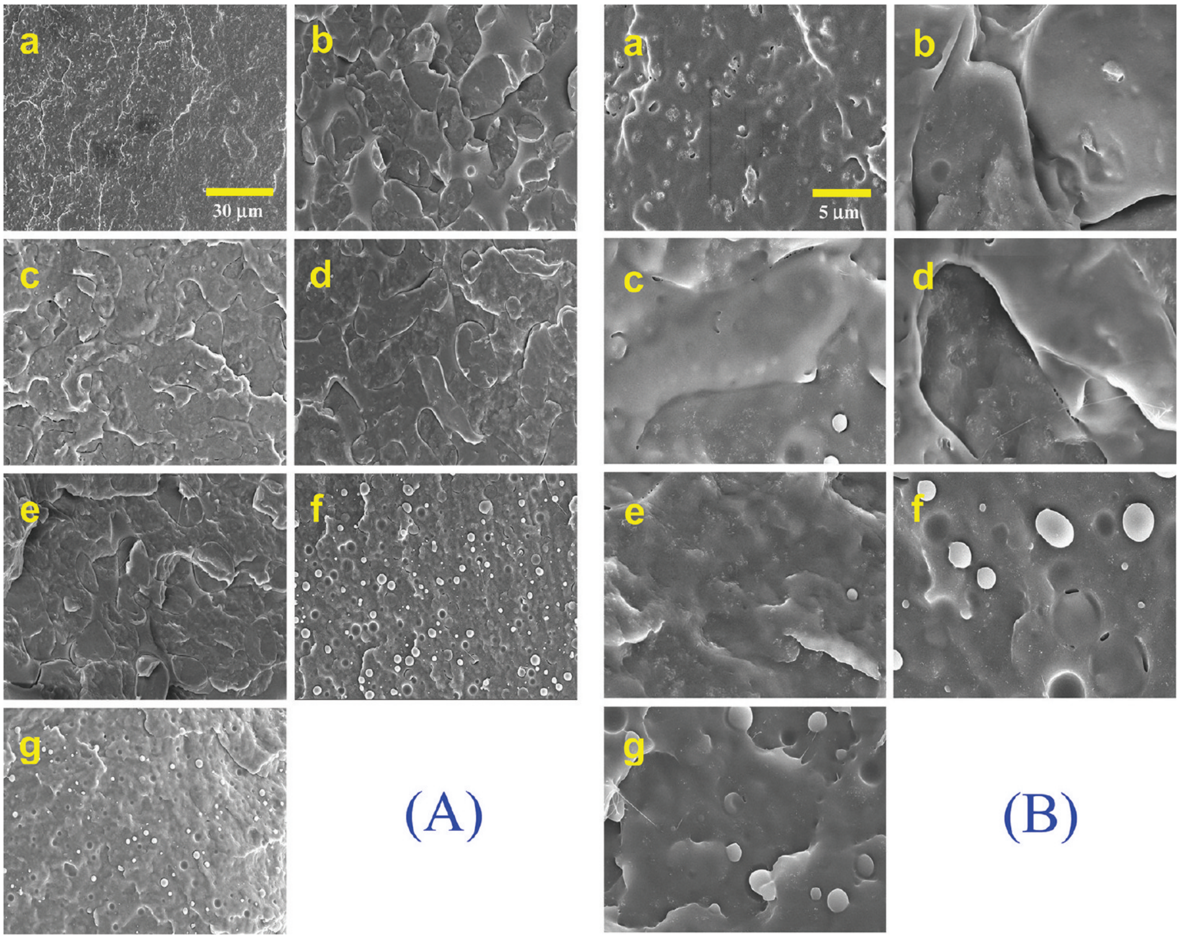

Figure 5. SEM micrographs for PLA/PCL/A-MWCNT composites with various PLA/PCL ratios. (a) 90/10, (b) 70/30, (c) 60/40, (d) 50/50, (e) 40/60, (f) 30/70, (g) 10/90. A-MWCNT content in PLA/PCL/A-MWCNT composites is 1.0 wt %. The scale bar in a of A representing 30 μm is applied to all other micrographs in A. The scale bar in a of B representing 5 μm is applied to all other micrographs in B.

A-MWCNT composites with PCL compositions of 70−90 wt %. Again A-MWCNTs selectively disperse in PCL phase domains, no matter that PCL forms dispersed or continuous phases. For the composite with PCL composition of 10 wt %, A-MWCNTs locate mainly in the PCL phase domains. Selective localization of A-MWCNTs in PCL phase domains is obvious for all the composites. The possible reasons are either A-MWCNTs have an intrinsic interfacial activity responsible for decreasing PLA/PCL interfacial tension or A-MWCNTs increase the PCL melt viscosity, providing a barrier to the phase coalescence process.[10] Analysis on the morphologies of PLA/PCL/A-MWCNT composites with different A-MWCNT contents (see Figure 2) is not in favor of the effect of interfacial activity,[27] which is different from the PC/PMMA/clay and PCL/PEO/clay composite systems.[30,31] Therefore, A-MWCNTs more likely increase the PCL melt viscosity, thus, perturbing the phase coalescence process. Compared with PLA/PCL 70/30 blend showing the morphology of many droplet-like minor PCL phase domains dispersing in PLA continuous phase (Figure 4b), PLA/PCL/A-MWCNT composite with PCL composition of 30 wt % shows much different morphology with more of the elongational PCL phases of larger sizes coexisting with elongational PLA phases (Figure 5Ab), which is considered to result from the increased PCL melt viscosity due to inclusion of A-MWCNTs, reducing the viscosity ratio between PLA and PCL melts.

It should be further noted that the added A-MWCNT content of 1.0 wt % for PLA/PCL/A-MWCNT composites with PCL compositions higher than 30 wt % is above the rheological percolation contents for the composites in this study (see the Supporting Information). Even higher A-MWCNT contents in the PCL phase domains can be obtained for PLA/PCL/A-MWCNT composites when introducing PLA component, because A-MWCNTs selectively accumulate into PCL phase domains, which makes local A-MWCNT contents rising even more above the percolation content. This will provide to the composites obviously enhanced electrical conductivities, as will be described in the next section.

Morphological Dependence of Electrical Conductivity. Polymer composites filled with increasing content of conductive fillers can show an electrical percolation behavior. It has been established that an essential condition for the conductivity of conductive fillers-contained composites is double percolations; that is, the conductive fillers must surmount its percolation threshold within the polymer (the first percolation), and the conductive fillers-contained polymer composites must undergo percolation in the matrix, maintaining connectivity within the blend (the second percolation). Electrical conductivity measurements reveal that the conductivity of blends is strongly related to the morphology.[32,33] Figure 6 shows the change in volume conductivity with PCL composition for PLA/PCL/A-MWCNT composites. The

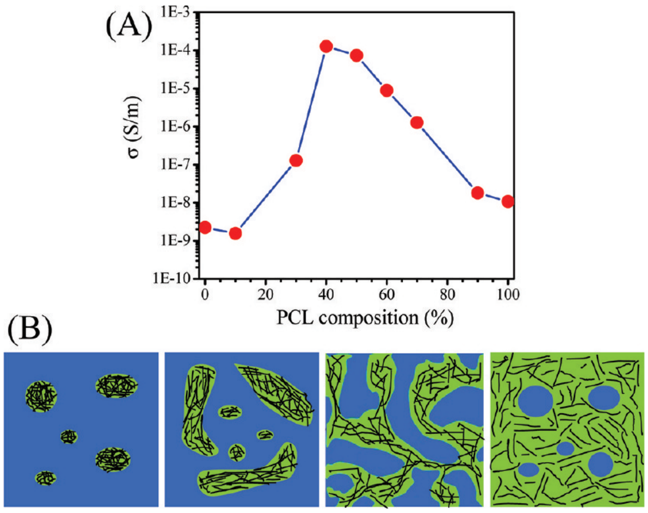

Figure 6. (A) Change in electrical conductivity, σ, with PCL composition for PLA/PCL/A-MWCNT composites with A-MWCNT content of 1.0 wt %; (B) schematic indicating corresponding morphological changes for PLA/PCL/A-MWCNT composites, in which blue regions represent PLA phase, green regions represent PCL phase, and black lines represent A-MWCNTs.

schematic shown in Figure 6B has been derived in an attempt to describe the conductivity change on the basis of the morphological observation by SEM (Figure 5). As for neat PLA and PCL, the conductivities are lower than 1×10^{-10} S/m. With addition of 1.0 wt % A-MWCNTs, the conductivities for PLA/A-MWCNT and PCL/A-MWCNT composites rise above 1×10^{-9} S/m. The relatively less enhancement of conductivity for PLA/A-MWCNT composites than that for PLA/P-MWCNT composites by Yoon et al. with addition of the same content MWCNTs is due to the A-MWCNT surface functionalization.[34] Furthermore, that the conductivity increases with PCL composition (addition of 1.0 wt % A-MWCNTs) depends on the morphologies. For PLA/PCL/A-MWCNT composite with PCL composition of 10 wt %, the conductivity does not show an obvious change compared with PLA/A-MWCNT composite, because A-MWCNTs are located mostly in the dispersed PCL phase domains, rather than in the continuous PLA matrix phase. Though the first conducting percolation is reached,[22] PCL phase domains are insulated by PLA continuous phase, leading to less effectively conducting. For PLA/PCL/A-MWCNT composite with PCL composition of 30 wt %, conductivity becomes higher than that with PCL composition of 10 wt %, because parts of PCL form continuous elongational phases, enabling more connections among them; however, there exist also the dispersed PCL phase domains, and thus, the second percolation is not reached. As PCL composition further increases to 40 and 50 wt %, the conductivities of the composites are far higher by about 3–4 orders than that with PCL composition of 30 wt %, indicating the formation of A-MWCNT percolation networks for efficient electron transportation. The stepwise increase of conductivity results from the formation of interconnected structure of A-MWCNTs, regarding as reaching above the electrical percolation threshold. This infers that a high percentage of electrons are permitted to flow through the specimen due to a creation of interconnecting conductive pathway. As for the composite with PCL composition of 60 wt %, a large quantity of PCL dilutes A-MWCNTs, decreasing local A-MWCNT content in PCL phase domains compared with the composite with PCL composition of 50 wt %, resulting in the local A-MWCNT content possibly below the first percolation value, and accordingly the conductivity decreases. Upon further increasing PCL compositions to 70 and 90 wt %, the effective local A-MWCNT contents in PCL phase domains are further reduced for a given overall A-MWCNT content in the composites, thereby, the conductivities are further decreased. To summarize, the effective A-MWCNT content in the PCL phase domains deceases with increasing PCL composition. On the other hand, even higher A-MWCNT contents in the PCL phase domains can be obtained for PLA/PCL/A-MWCNT composites when introducing PLA component, because A-MWCNTs selectively accumulate into PCL phase domains, which makes local A-MWCNT contents rising even more above the percolation content for the enhanced electrical conductivity. Therefore, the observed variation of electrical conductivity for PLA/PCL/A-MWCNT composites is the result of phase morphologies and effective A-MWCNT contents, and both effects contribute to the formation of the conductive path. The above results demonstrate a potential use of such cocontinuous blend matrix as a basic material for production of conductive and/or antistatic polymer membranes.[35,36]

4. CONCLUSIONS

The effects of addition of acid-oxidized MWCNTs (A-MWCNTs) on the phase morphology and electrical conductivity have been investigated for PLA/PCL/A-MWCNT composites with various PCL compositions ranging from 5 to 90 wt %. For the melt compounded PLA/PCL/A-MWCNT composites A-MWCNTs are homogeneously and selectively located in PCL phase domains. Addition of small contents of A-MWCNTs (0.5–6 wt %) into the composites with a fixed PLA/PCL ratio of 95/5 reduces the sizes of PCL phase domains enriched with A-MWCNTs, with some A-MWCNTs appearing at phase interfaces, which indicates that A-MWCNTs effectively prevent from coalescence of the dispersed PCL phase domains. For the PLA/PCL/A-MWCNT composites added with 1.0 wt % A-MWCNTs with various PCL compositions, the maximum electrical conductivity is observed at the PCL composition of 40 wt %, which can be well explained by the formed cocontinuous phase domain structures with the interconnected A-MWCNT structure. The observed variation of electrical conductivity for PLA/PCL/A-MWCNT composites is the result of phase morphologies and effective local A-MWCNT contents, and both effects contribute to the formation of the conductive path. This study infers a potential use of the blends with cocontinuous morphology for production of conductive and/or antistatic polymer materials.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

A high-magnitude SEM micrograph for PLA/PCL/A-MWCNT (95/5/0.5) composite and changes of storage modulus (G'), loss modulus (G''), loss tangent (tan δ), and complex viscosity ($|\eta^*|$) with frequency for PLA/PCL/A-MWCNT composites with A-MWCNT content of 1.0 wt %. This material is available free of charge via the Internet at http://pubs.acs.org.

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