

The Plasticizer-Assisted Formation of a Percolating Multiwalled Carbon Nanotube Network in Biodegradable Poly(L-lactide)

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Received 9 January 2011; accepted 8 April 2011

DOI 10.1002/app.34658

Published online 22 August 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: A plasticizer, polyethylene glycol (PEG), was used to disperse multiwalled carbon nanotubes (MWCNTs) in biodegradable poly(L-lactide) during one-step melt mixing. Incorporation of PEG significantly promotes the formation of a percolating MWCNT network in the plasticized composites, as revealed by rheological measurements and morphological observations. It, in turn, results in the retarded glass transition and cold crystallization behaviors in these plasti-

cized composites as a result of constrained chain relaxation. It is believed that noncovalent wrapping of MWCNTs by PEG is responsible for the improved affinity between MWCNTs and the poly(L-lactide) matrix. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 1843–1847, 2012

Key words: multiwalled carbon nanotubes; poly(L-lactide); plasticizer; percolating network

INTRODUCTION

As an excellent filler, carbon nanotubes (CNTs) can impart polymer composites with superior mechanical, electrical, and thermal properties.^{1–6} In particular, formation of a percolating CNT network in the polymer matrix, mostly depending on the dispersion of CNTs, is responsible for the significant conductivity enhancement as well as nonterminal rheological behaviors. Thus, achieving an appropriate dispersion of inorganic CNTs in the polymer matrix is a key issue to ensure low percolation threshold in parallel with high mechanical performance.^{7,8}

However, the intrinsic incompatibility between CNTs and polymers usually gives rise to large agglomerations of CNTs in the composites. To avoid it, extensive efforts have been carried out in the past studies. Surface modification of CNTs, via chemical grafting with some amount of organic moieties at defect sites, is an important approach to improve the dispersion as well as the mutual interactions between CNTs and polymer matrix.^{9–11} Meanwhile,

a surfactant or a copolymer, which has affinity towards both CNTs and polymers, is usually used to assist the dispersion of CNTs in the polymer matrix without chemical reaction.^{4,12–14} In addition, different preparation methods, such as melt mixing, in situ polymerization, coagulation, and so on, are also explored to tailor the dispersion of CNTs in the composites.^{15–17}

To date, modification of biodegradable poly(L-lactide) (PLLA) with CNTs has attracted much interest.^{18–22} Similar to other polymers, functionalization of CNTs or adopting suitable preparation methods is necessary for the good dispersion of CNTs in the PLLA, which in turn gives rise to low percolation threshold for electrical and rheological properties.^{21,22} On the other hand, blending of semi-flexible PLLA with a plasticizer, such as PEG, is critical to improve its flexibility, as a result of good miscibility between these two components.^{23,24} Inspired by the noncovalent wrapping of CNTs with surfactants in other polymer composites, it is expected that PEG could take the similar effect and assist the dispersion of CNTs in the PLLA matrix, which is the aim of this study.

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Contract grant sponsor: National Natural Science Foundation of China; contract grant numbers: 50973017, 21004010, 20704006.

Contract grant sponsor: Project of Jiangxi Provincial Department of Education; contract grant number: GJJ08295.

Journal of Applied Polymer Science, Vol. 123, 1843–1847 (2012)
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EXPERIMENTAL

Materials

The PLLA, supplied by Natureworks, had a melt flow index of about 75 g/10 min and a relative viscosity of 2.5, respectively. PEG with a molecular

weight of 4000 g/mol was purchased from Sino-pharm Chemical Reagent. MWCNTs were obtained from Chengdu Institute of Organic Chemistry, Chinese Academic of Science. Before use, the pristine MWCNTs were first treated in a 0.3 wt % KMnO_4 solution with 2 : 1 concentrated $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ as mixed solvents for 40 min using bath sonication method at a frequency of 40 kHz, followed by repeated washing in the distilled water until the pH value of the solution was up to 7.

Melt blending and sample preparation

PLLA/MWCNT composites with and without PEG were melt-blended in an internal mixer at 190°C for 8 min through one-step approach. Note that in the plasticized composites, the ratio of PLLA to PEG was 9 : 1, and the content of MWCNTs was weighed by the total amount of PLLA and PEG. Virgin PLLA and plasticized PLLA/PEG = 9/1 without MWCNTs were also subjected to the same processing procedure mentioned above. For simplicity, plasticized and virgin composites containing 3 wt % MWCNTs, for instance, were labeled as P3 and V3, respectively. To prepare samples for dynamic mechanical analysis (DMA) and thermal analysis (DSC), as-mixed composites were compression molded in a hot press at 190°C under a pressure of 5 MPa, followed by quenching into ice water.

Structural characterizations

Rheological properties were measured on disks (1.5 mm thickness \times 25 mm diameter) by a stress controlled rheometer, AR2000EX (Rheometrics Scientific, NJ), using 25 mm diameter parallel plates at 190°C under a nitrogen atmosphere. Small-amplitude oscillatory shear (SAOS) was performed within the linear viscoelasticity region. The dispersion morphology of MWCNTs in the matrix was evaluated by an optical microscope and a Hitachi S3400 scanning electron microscope, respectively. Dynamic mechanical measurements were performed in the tensile mode using a TA instruments Q800 Dynamic Mechanical Analyzer at a heating rate of $2^\circ\text{C}/\text{min}$, a frequency of 1 Hz, and a strain of 0.15%, respectively. Thermal behaviors were evaluated by heating samples of about 7 mg from 30 to 200°C at $10^\circ\text{C}/\text{min}$ using NETZSCH DSC 204 under a nitrogen atmosphere.

RESULTS AND DISCUSSION

Figure 1 shows the rheological properties of virgin and plasticized PLLA/MWCNT composites with various MWCNT contents. In both types of composites, the storage modulus, G' , and loss modulus, G'' , increase with MWCNT content especially in the ter-

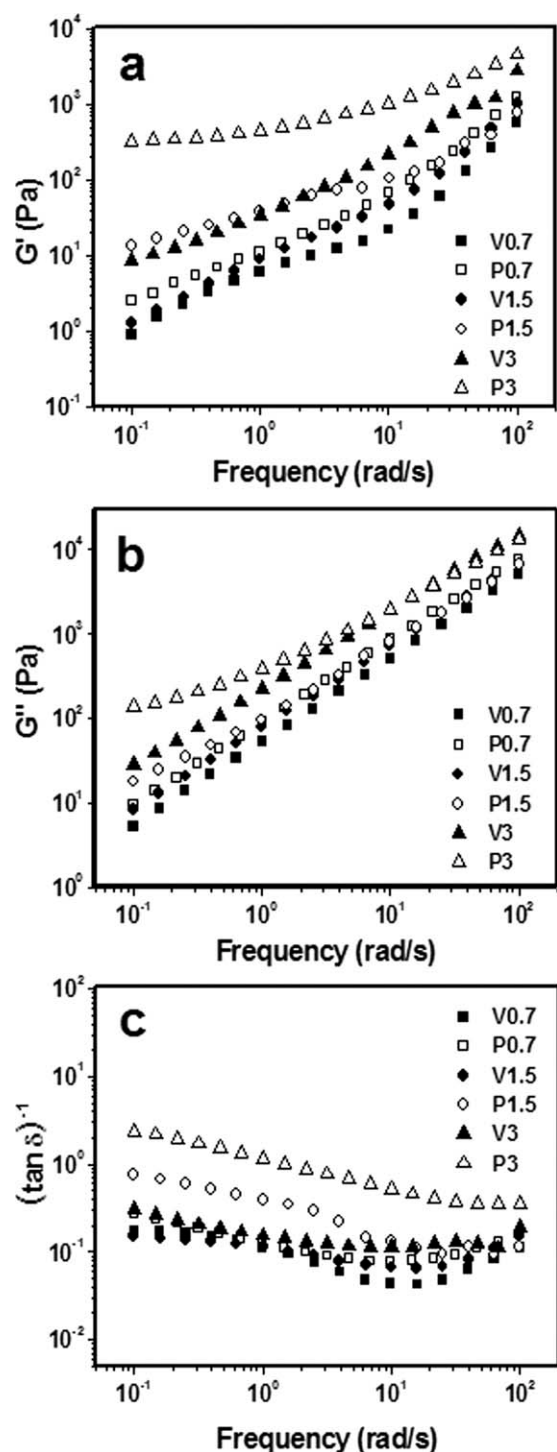


Figure 1 Frequency dependence of storage modulus (a), loss modulus (b), and inverse loss tangent (c) in the plasticized and virgin PLLA/MWCNT composites.

minal zone, irrespective of addition of PEG. On the other hand, at the same MWCNT loading the moduli become higher in the plasticized composites than those of virgin counterparts. In particular, in the terminal zone, the moduli become nearly independent of frequency, an indicator of solid-like viscoelastic behavior, as the MWCNT loading is beyond 1.5 wt

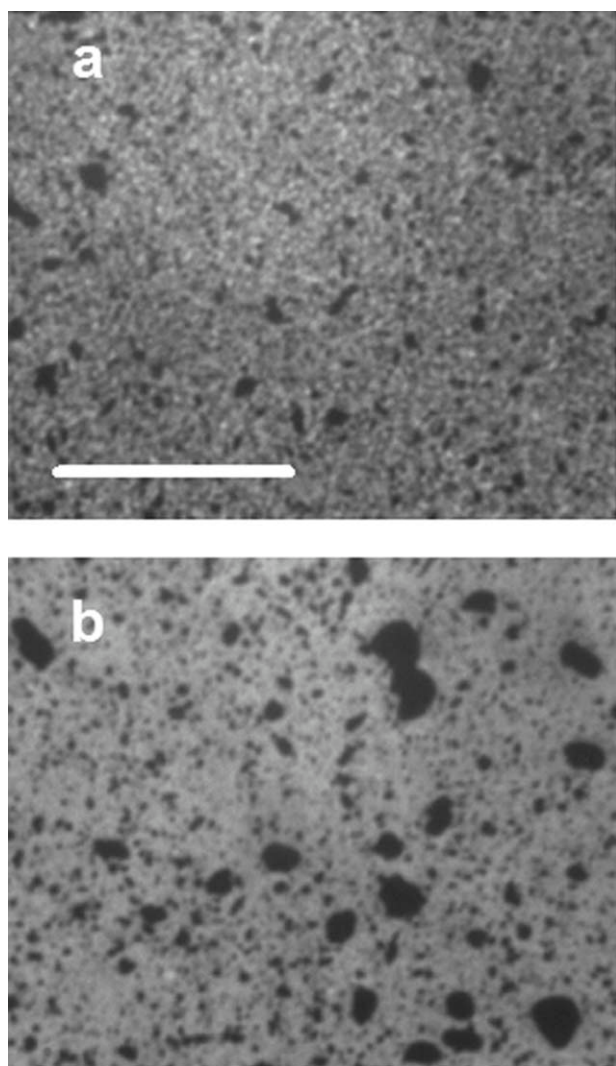


Figure 2 Optical micrographs revealing the dispersion of MWCNTs in the plasticized (a) and virgin (b) composites with 3 wt % MWCNTs loading. The scale bar is 100 μm .

% in the plasticized composites. Additional insight into solid-like viscoelastic behavior can be deduced from the inverse loss tangent, G'/G'' , as shown in Figure 1(c). In the terminal zone, the inverse loss tangent increases significantly in the plasticized composite with high MWCNT loading.

As demonstrated in the past studies,^{3,4,12,21} this nonterminal behavior in the composites is originated from the formation of a percolating MWCNT network that imposes significant constraints on the molecular motions of PLLA. Thus, it strongly suggests that incorporation of plasticizer PEG is helpful for the dispersion and network formation of MWCNTs in the PLLA matrix during one-step melt mixing. Moreover, for the plasticized composites, the rheological percolation threshold is close to 1.5 wt %, which is nearly identical to that observed in the polylactide composites filled with five-armed star polylactide grafted MWCNTs.²¹

The dramatic effect of plasticizer PEG on the dispersion and network formation of MWCNTs in the PLLA matrix is further demonstrated by the morphological observations. Figure 2 shows the typical optical micrographs of virgin and plasticized PLLA composite containing 3 wt % MWCNTs. Large agglomerates of MWCNTs are presented in the virgin PLLA composites, whereas relative homogenous distribution of MWCNTs is observed in the ones plasticized by PEG. Moreover, a close inspection by scanning electron microscopy, as shown in Figure 3, reveals that at submicron scale the MWCNTs in the plasticized PLLA composites tend to interconnect with each other and form a network structure (the

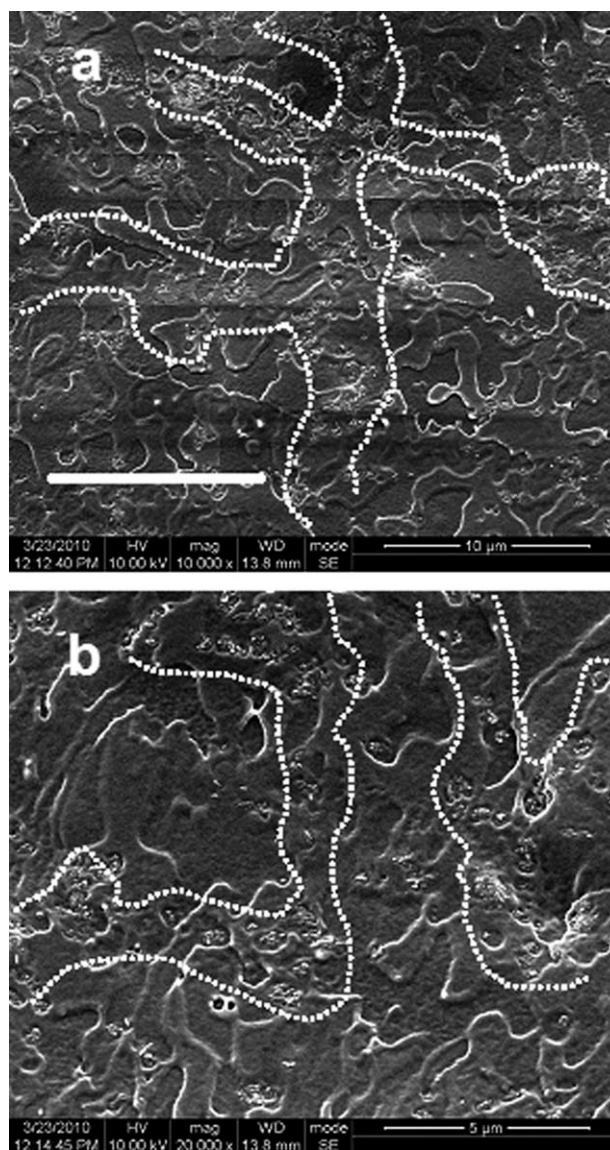


Figure 3 Morphological observation of formation of a MWCNTs network structure (illustrated by the white dashed lines) in the plasticized composites with 3 wt % MWCNTs loading at different magnification. The scale bar corresponds to 10 and 5 μm in (a) and (b), respectively.

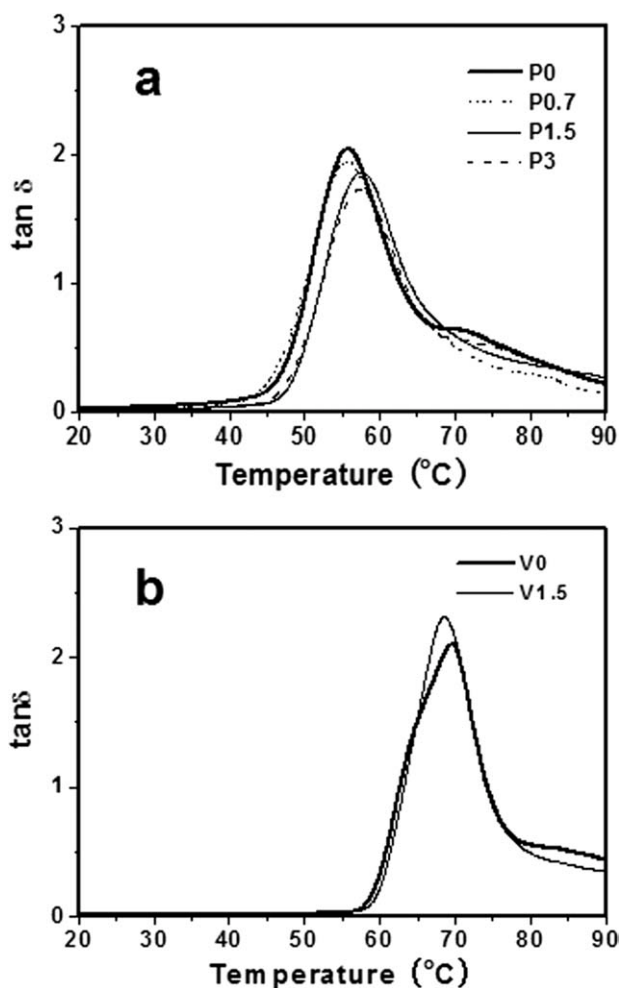


Figure 4 Temperature dependent loss factor in the plasticized (a) and virgin (b) composites.

regions marked by the white dashed lines in Fig. 3). It further provides direct evidences regarding that PEG can assist the formation of a MWCNT network in the PLLA matrix, consistent with above rheological results.

Figure 4 illustrates the loss factor of virgin and plasticized PLLA/MWCNT composites, revealing the change of glass transition behavior with respect to the MWCNT loadings. As an effective plasticizer for PLLA, incorporation of PEG does enhance the molecular motions, manifested by the significant decreasing of glass transition temperature in the plasticized PLLA.²³ On the other hand, in the plasticized composites adding MWCNTs postpones glass transition behavior, whereas its loading is and beyond 1.5 wt %. The glass transition temperature in these plasticized composites is increased by about 2°C with respect to that of plasticized PLLA itself, deduced from the peak of the $\tan \delta$ curves. The retarded glass transition behavior corresponds to the reduced segmental motions, as a result of the formation of a percolating MWCNT network that can

restrain the chain relaxation of PLLA matrix. On the contrary, in the virgin composites, the glass transition temperature keeps nearly constant even with 1.5 wt % MWCNT loading.

Figure 5 shows the heating traces in the plasticized PLLA/MWCNT composites from the glassy state. Note that the initial samples are amorphous, as indicated by X-ray diffraction results (not shown). Upon heating enhanced molecular mobility can give rise to crystallization of PLLA matrix, which is termed as cold crystallization. It is indicated that cold crystallization temperature is first decreased and then increased again with respect to MWCNT contents. The above change of cold crystallization behavior in the plasticized PLLA/MWCNT composites is resulted from the combined effects of nucleation and diffusion controlled growth processes. On the one hand, the nucleation ability of MWCNTs towards PLLA matrix can give rise to the decreasing of cold crystallization temperature,^{21,25,26} which could become significant with the MWCNT

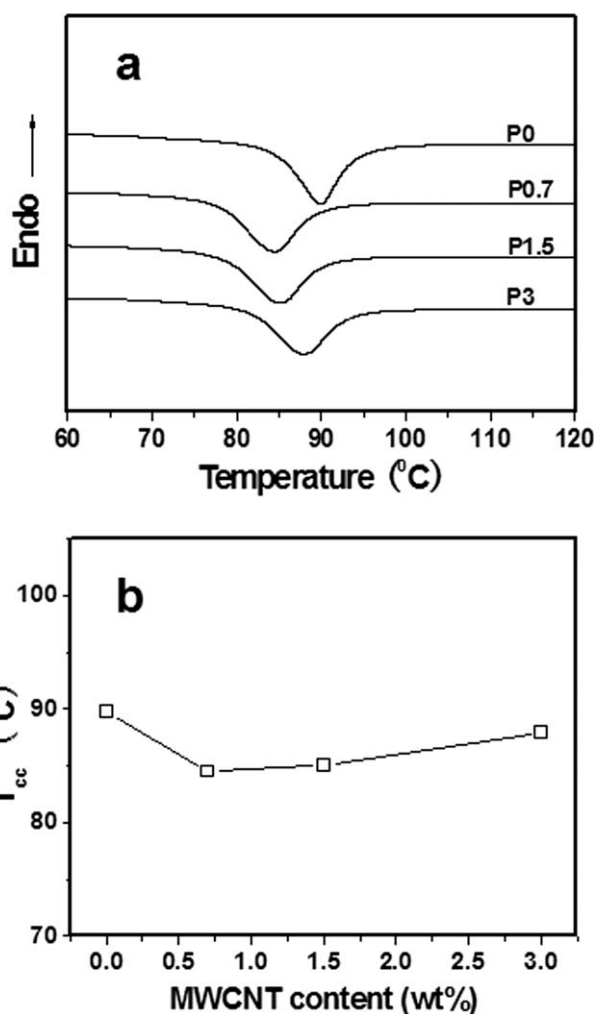


Figure 5 Heating traces (a) and deduced cold crystallization temperature T_{cc} (b) in the plasticized composites.

loadings. As argued by other researchers,²¹ on the other hand, formation of a percolating MWCNT network can suppress the molecular motions, as demonstrated by above rheological and dynamic mechanical properties, and thus acts as a hindrance to retard the cold crystallization of PLLA matrix, which in turn results in the increasing of cold crystallization temperature at high MWCNT loading.

In combination with above results, it is unambiguously demonstrated that the plasticizer PEG indeed assists the formation of a percolating MWCNT network in the PLLA matrix during melt mixing. It is expected that PEG could be more compatible with MWCNTs than PLLA matrix, whereas the polarity and molecular weight are taken into account. Thus, during melt mixing the surface of MWCNTs tends to be noncovalently wrapped by PEG, though possible chemical reactions are absent, and becomes more hydrophobic, which in turn improves their affinity with PLLA matrix. In this context, the plasticizer PEG takes the similar effect as surfactants, for instance sodium dodecyl sulfate assisting the dispersion of CNTs in the polyethylene matrix.^{4,12} In the latter, the CNTs are first dispersed in water with aid of surfactants, followed by spaying the suspended solution onto the fine polyethylene powders before melt processing. Obviously, the procedures using surfactants are more time-consuming and uneconomical, as compared with one-step mixing of MWCNTs with PEG and PLLA in our case.

CONCLUSIONS

The results presented in this work clearly illustrate that adding plasticizer PEG is indeed beneficial for the dispersion of MWCNTs in the PLLA matrix during melt mixing. It, in turn, gives rise to the formation of a percolating MWCNT network at relative low loadings, manifested by the nonterminal rheological properties and retarded glass transition and cold crystallization behaviors. Though in nature PEG takes the similar effect as surfactants to modify the surface of CNTs by noncovalent bonding interactions, our findings offer a simple and economic method to disperse MWCNTs in polymer matrix through one-step melt mixing.

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