Ultralow Percolation Threshold in

Poly(L-lactide)/Poly(ε-caprolactone)/Multi-Wall Carbon Nanotubes Composites

with a Segregated Electrically Conductive Network

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1. Thermodynamic and kinetic analysis for the localization of MWCNTs in the PLLA/PCL/MWCNTs composites

The localization of MWCNTs in the PLLA/PCL/MWCNTs composites was first estimated by calculation of the wetting coefficient (ω)

$$\omega = \frac{\gamma_{MWCNT-b} - \gamma_{MWCNT-a}}{\gamma_{ab}}$$

where $\gamma_{MWCNT-a}$ and $\gamma_{MWCNT-b}$ are the interfacial energy respectively between MWNTs and component a, between MWNTs and component b, respectively, and γ_{ab} is the interfacial tension between the two components. If the wetting coefficient is higher than 1, the filler will preferentially be located in component a; if the wetting coefficient is lower than -1, the filler will preferentially be located in component b, and if the wetting coefficient is between -1 and 1, the filler will be located at the interface between the two components.

In this work, the PLLA granules coated with PCL or PCLNT at 100 ^{o}C. Thus, it is necessary to extrapolate the surface energies towards the coating temperature. In

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order to obtain the high temperature data, the polymer polarity is assumed to be independent on the temperature. The surface parameter values (100 ^{o}C) of PLLA and PCL (see Table S1) were extrapolated from the experimental 25 ^{o}C values using the temperature coefficients of 0.06[S1] and 0.058 [S2] mN·m^{-1}·K^{-1}, respectively.

Table S2 shows the interfacial energies of the sample pair. The wetting coefficient of PLLA/PCL/MWCNTs composites at both 25 ^{o}C and 100 ^{o}C are shown in Table S3. All the wetting coefficient values are lower than -1, which means that the MWCNTs are preferably to locate in PLLA phase both at 25 ^{o}C and 100 ^{o}C.

Table S1 Surface tensions of pure PLLA and pure PCL at 25 ^{o}C and 100 ^{o}C which extrapolated from values at 25 ^{o}C. The surface tensions of MWCNTs were obtained from the reference[S3].

Samples	Total (γ),(mN/m)	dispersive part (γ^d), (mN/m)	polar part (γ^p), (mN/m)
MWCNTs	27.8	17.6	10.2
PLLA (25 ^{o}C)	43.2	39.2	3.9
PLLA (100 ^{o}C)	38.7	35.2	3.5
PCL(25 ^{o}C)	38.4	36.5	1.9
PCL(100 ^{o}C)	34.1	32.4	1.7

Table S2 The calculated values of interfacial energies for various sample pairs

	Interfacial energies(mN/m) Calculation methods	
Sample pair	harmonic	geometric
PLLA (25 ^{o}C)/MWCNTs	11.1	5.9
PLLA (100 ^{o}C) /MWCNTs	9.1	4.8
PCL (25 ^{o}C)/MWCNTs	12.3	6.7
PCL (100 ^{o}C) /MWCNTs	10.5	5.8
PCL (100 ^{o}C)/ PLLA (100 ^{o}C)	0.7	0.4
PCL(25 ^{o}C) /PLLA (25 ^{o}C)	0.8	0.4

Table S3 Wetting coefficient evaluated according harmonic mean equation, geometric mean equation

| | Wetting coefficient Calculation methods | |
Materials	harmonic	geometric
PLLA (25 $^{\circ}$C)/PCL (25 $^{\circ}$C)/MWCNTs	-1.5	-2.0
PLLA (100 $^{\circ}$C)/PCL (100 $^{\circ}$C)/MWCNTs	-2.0	-2.5

In fact, the PCL coated PLLA granules at 100 $^{\circ}$C where the PLLA phase is solid. Thus, the MWCNTs can only locate in PCL phase. Because the PCL is completely melted and shows low viscosity at 100 $^{\circ}$C. The PCL chains are more readily to diffuse around and into the MWCNTs aggregates compared with that of the PLLA chains at 100 $^{\circ}$C and, the MWCNTs are incorporated inside the low viscous PCL phase preferentially and finally trapped inside it. Therefore, the MWCNTs actually located in PCL phase by the kinetic aspects in our case.

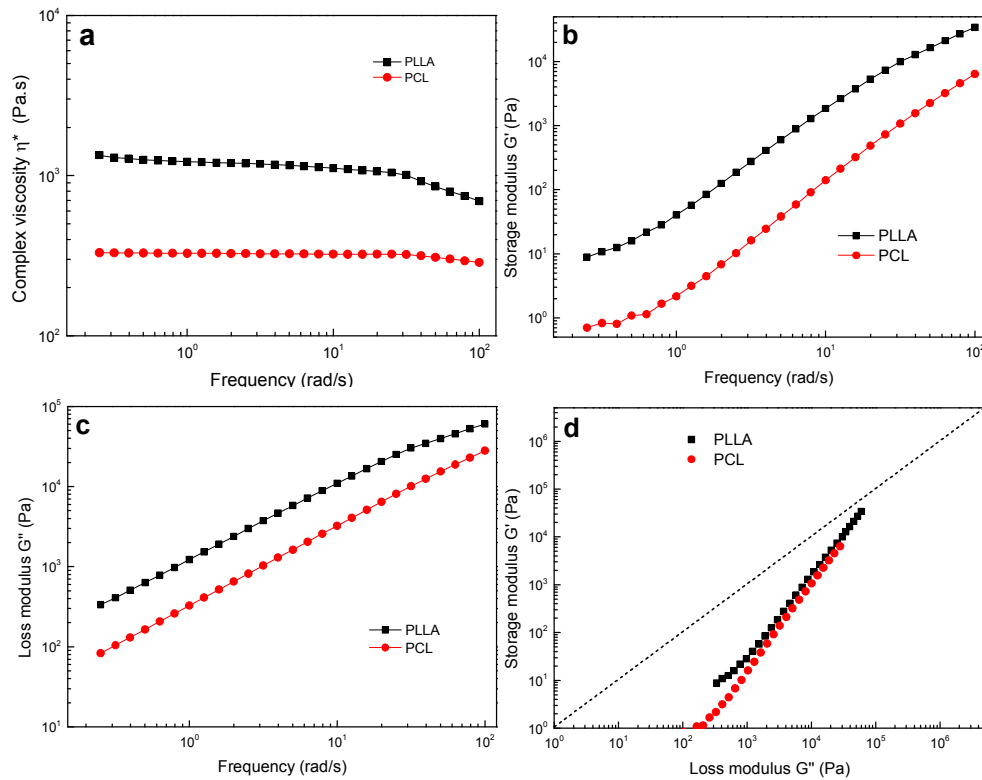## 2. Rheological properties of pure PLLA and pure PCL

Figure S1 (a) Complex viscosity η^*, (b) storage modulus G' and (c) loss modulus G''

of the pure PLLA and pure PCL as a function of frequency at 160 ^{o}C, (d) G' as a

function of G'' of pure PLLA and pure PCL.

References

[S1] Katada, A.; Buys, Y. F.; Tominaga, Y.; Asai, S.; Sumita, M. Relationship between electrical resistivity and particle dispersion state for carbon black filled poly (ethylene-co-vinyl acetate)/poly (L-lactic acid) blend. *Colloid Polym. Sci.* **2005**, *284*, 134-141.

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[S3] Barber, A. H.; Cohen, S. R.; Wagner, H. D. Static and dynamic wetting measurements of single carbon nanotubes. *Phys. Rev. lett.* **2004**, *92*, 186103.