

Preparation of High Performance Conductive Polymer Fibres from Double Percolated Structure

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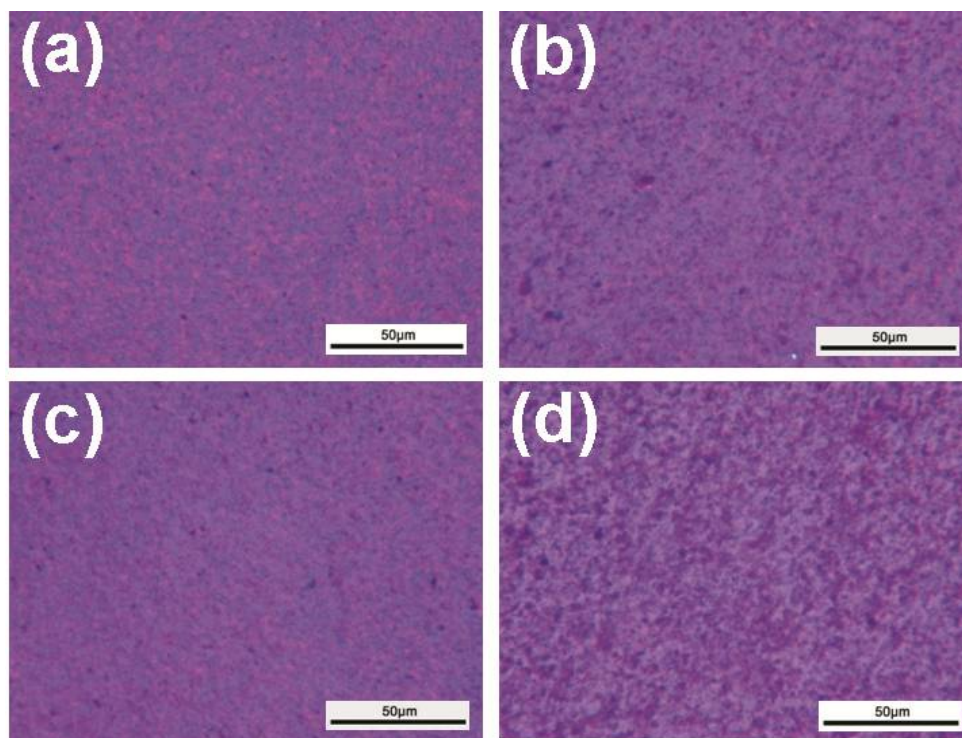


Fig. S1 Optical microscope micrographs of PE-NT composites (a) PE-1NT, (c) PE-3NT and PP/PE-NT blends (b) P364, (d) P546

To characterize the dispersion status and distribution of CNTs in these systems, optical microscope study was carried out (see Fig. S1). It is observed that most of the CNTs are well dispersed in the PE matrix without any obvious agglomeration.

Comparing Fig. S1c (PE-3NT) with Fig. S1d (P546), the same overall amount of CNT is contained in these two systems; but the distribution of CNT is obviously different. In Fig. S1d, the dark area (PE-NT phase) formed a continuous path in the brighter phase (neat PP). Such a structure is entitled as double percolation structure. In this structure, CNTs are mostly distributed in the PE phase, where the CNT are

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relatively homogeneously dispersed in the same manner as in the binary composites (see Fig. S1c). Using this method, conductive polymer blends can be fabricated using much less conductive filler. However, both CNT conductive networks in PE-NT phase and the continuity of this phase in the blends are essential for maintaining a conductive network through such a double-percolated structure.

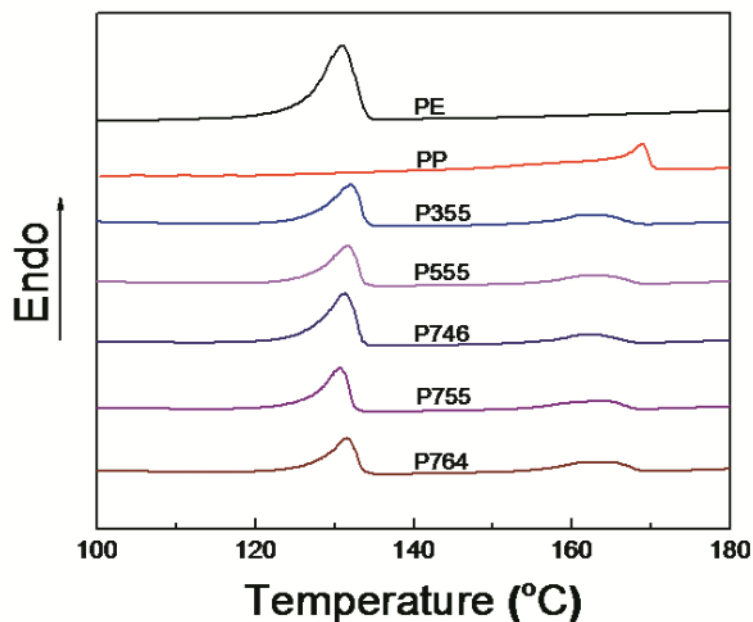


Fig. S2 DSC heating thermogram of PP/PE-NT blends.

Thermal annealing at 150 °C for 30 mins is used to recover the continuous PE phase and conductive CNT networks in the blends (See Fig. S3). For specimens with a draw ratio of 3, the resistivity after annealing is slightly lower than that of isotropic specimens. It is caused by the increased local contacts density between local conductive networks provided by the relaxation of oriented CNT bundles during annealing. Similar phenomenon has been reported by us elsewhere in a multi-layered bicomponent system¹⁻³. It should be noted that the reformation of conductive network in the blends requires two conditions: the reformation of continuous PE-NT phase, and the reformation of CNT conductive network. In the specimens with a draw ratio of 3, the PE-NT phase is not significantly destructed. Therefore, these specimens behave like multi-layered bicomponent tape where the conductive phase is always continuous during drawing and annealing.

Nevertheless, the resistivity for the specimens with draw ratios of 6 or 10 is almost the same or slightly higher than that of the original isotropic specimens. It is believed that there are two reasons responsible for this: the not fully reversible PE-NT phase at higher draw ratios under current annealing condition, and the reformation of CNT network during relaxation of highly oriented CNT networks. Moreover, it is interesting to notice that the specimens containing more PE-NT phase at draw ratios of 6 and 10 (such as P746 in Fig. S3a) have resistivity closer to the ones from original isotropic specimens comparing with P755 and P764. As the stability of the PE-NT phase under deformation is higher for those containing more PE. In addition, the destruction and reformation of CNT network is also investigated through using blends with the same PP-PE ratio containing different amount of CNT (see Fig. S3b). The relaxation behavior of these blends at high draw ratios (6 and 10) is similar. In terms of reversibility of the conductive network during drawing and annealing, by comparing Fig. S3a with b, it can be concluded that the PE-NT blends behave similar with the multi-layered bicomponent tape (reported elsewhere¹⁻³) at draw ratio of 3 as the continuity of the PE-NT is mostly kept at such a low draw ratio. Nevertheless, the continuity of the PE-NT phase is destroyed at higher draw ratios (6 and 10), and it can not be fully repaired by annealing.

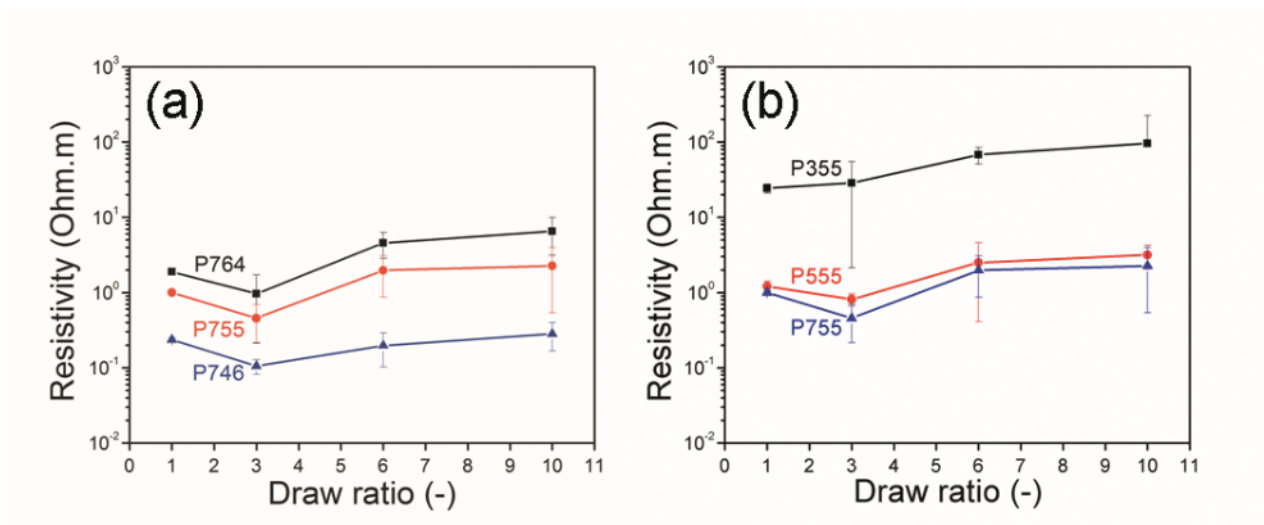


Fig. S3 The resistivity of samples after annealing (a) same PE-NT with different PP/PE-NT ratio (b) same PP/PE-NT ratio with different CNT content in PE-NT.

From the morphology of CNT network in these samples shown in Fig. S4, the density of CNT is obviously higher with higher PE-NT content. From the morphology of CNT, it can be concluded that the continuity is easier to be destructed at lower PE-NT content.

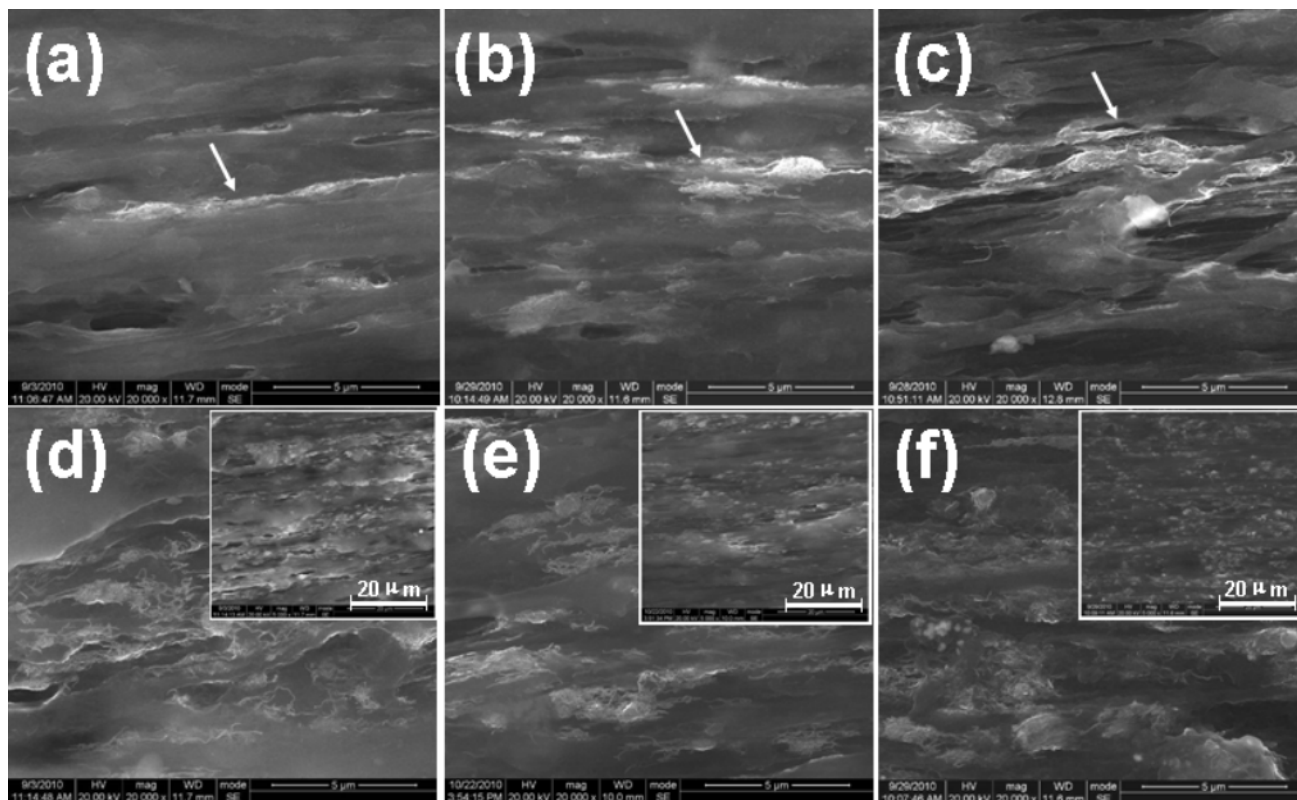


Fig. S4 SEM micrographs of solid state drawn tape ($\lambda=6$) of (a) P764, (b) P755, (c) P746 and solid state drawn plus annealed tape of (d) P764, (e) P755, (f) P746. Note that the inset pictures show the same specimen at a low magnification.

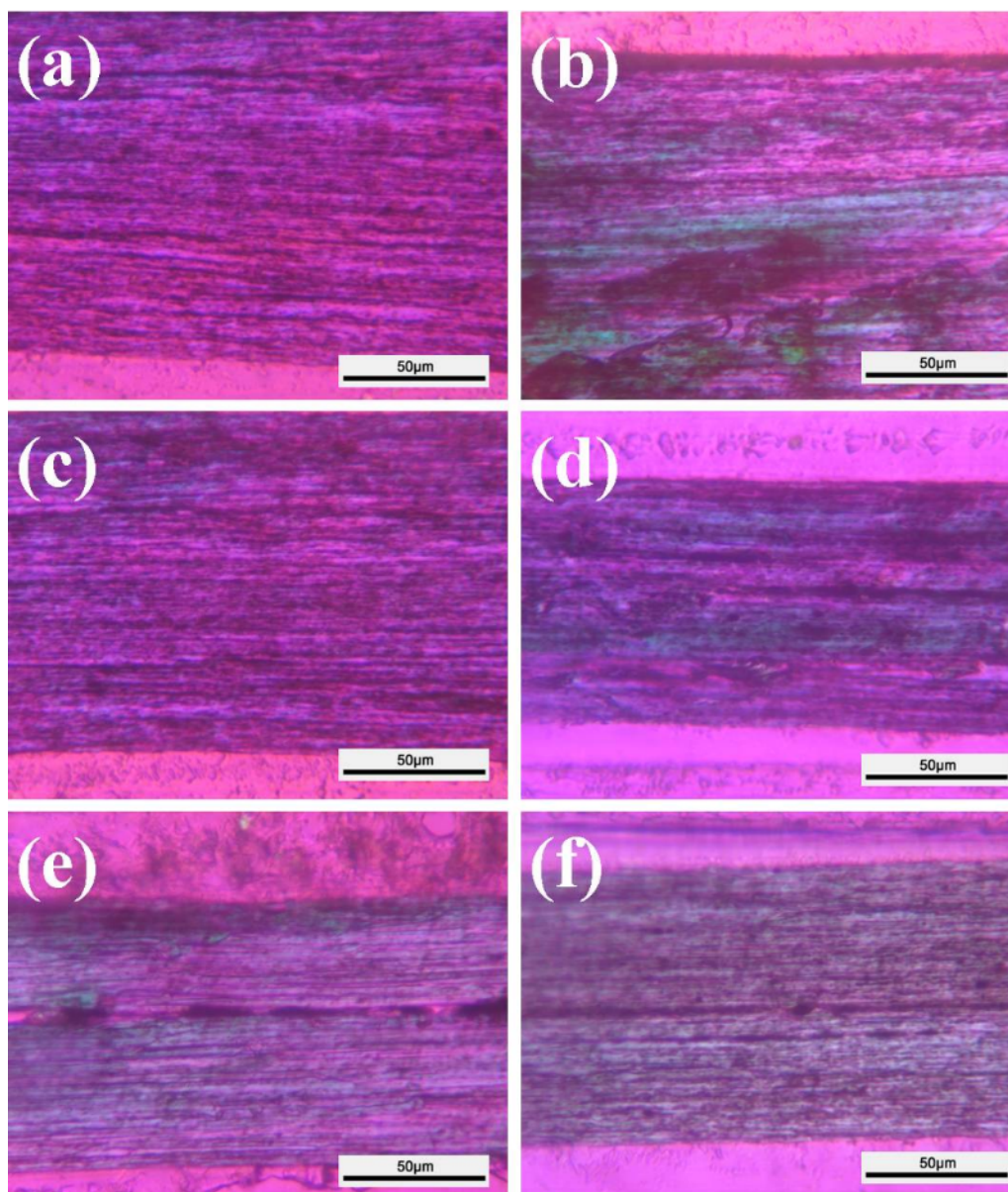


Fig. S5 Optical microscope micrographs of P764 along the drawing direction for solid state drawn tape (a) $\lambda=3$, (c) $\lambda=6$, (e) $\lambda=10$, and solid state drawn plus annealed tape (b) $\lambda=3$, (d) $\lambda=6$, (f) $\lambda=10$.

DSC study has been carried out to investigate the effect of drawing and annealing on the crystallinity of PP and HDPE. The results are summarized in Table S1. It is obvious to note that the drawing and annealing does not change the crystallinity of PE-NT phase. Furthermore, more experiment is carried out to investigate the effect of crystallinity on the conductivity (see Fig. S6 and Table S2). The crystallinity of PE-NT phase is changed from 29.5 % to 33.4 % (for P546) by annealing (at 100 °C) a quenched specimen. It was demonstrated in in-line electrical measurement that the electrical properties

of the sample is almost not changed. Therefore, the crystallinity of the specimen does not have significant effect on the conductivity.

Table S1 The crystallinity of the samples

Samples	P555-original	P555-drawn ($\lambda=10$)	P555-annealed ($\lambda=10$)
Delta H/J/g (PE/PP)	78.070 / 30.785	81.045 / 38.831	73.813 / 47.810
X_c/% (PE/PP)	26.6 / 14.7	27.7 / 19.1	25.2 / 23.5

* Standard heat enthalpy PE: 293J/g; PP: 209J/g.

Table. S2 The crystallinity of the samples

Smamples	P546-quenched	P546-annealed	P555-quenched	P555-annealed
Delta H/J/g (PE/PP)	86.533 / 31.751	97.966 / 36.093	74.325 / 42.614	72.628 / 42.401
X_c/% (PE/PP)	29.5 / 15.2	33.4 / 17.3	25.4 / 21.0	24.8 / 20.9
Peak/°C (PE/PP)	131 / 170	132 / 164	130 / 162	130 / 164

* Standard heat enthalpy PE: 293J/g; PP: 209J/g.

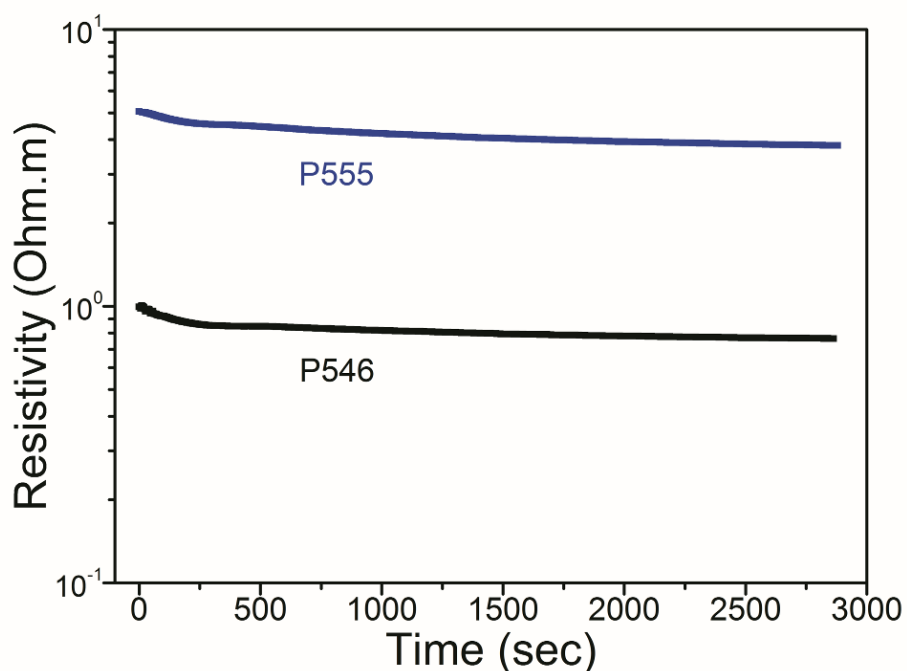


Fig. S6 In-line experiment of the annealing procedure at 100 °C.

REFERENCES AND NOTES

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