

Multifunctional Polymer Nanocomposites with Interface Engineered Nanostructures

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Abstract

This ongoing project is aimed at studying the effects of the interface between nanofillers and polymers in physical mixtures fabricated by traditional and innovative methods to explore the potential properties of polymer nanocomposites (PNCs). Chapter 1 is an introduction. In Chapter 2, we used a solvent extraction method to synthesize homogenous PNCs with magnetic properties to investigate the advantages and disadvantages of the PNCs with well dispersed nanofillers. The thermogravimetric analyzer (TGA) and microscale combustion calorimeter (MCC) revealed an enhanced thermal stability and reduced flammability. The observed monotonically decreasing complex viscosity indicated a strong shear thinning behavior in the PNCs. Chapter 3 presents a discontinuous structure of gold nanoparticles (Au NPs) on the surface of a sub-micrometer sphere polymer with a layer of alternative polymer film. A surface interaction is exhibited between the polymer spheres and the Au NPs. The real permittivity of the PNCs is much higher than that of the pure polymer spheres, and an improved thermal stability is obtained in the PNCs. The PNCs also possess a lower bandgap than that of the pure polymer sphere. Chapter 4 describes a study of carbon nanotubes (CNTs) coated on the surface of gelated soft Polypropylene (PP) powders, which were easily pressed together and formed a network structure in the hosting materials, leading to outstanding electrical properties. Chapter 5 is an extension of Chapter 4 to further investigate CNTs/ethylene/1-octene copolymers (EOCs) PNCs system. Chapter 6 concerns that microwave radiation as an environment-friendly method to enhance electrical conductivity of carbon nanotube (CNT) polymer nanocomposites (PNCs) without utilizing a solvent. Conclusions and future work are provided in Chapter 7.

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Chapter 1. Introduction

1.1. Multifunctional Polymer Nanocomposites (PNCs)

Polymers are large molecules or macromolecules composed of repeating structural units typically connected by covalent chemical bonds, which have been considered as excellent host matrixes for composite materials due to their light-weight, easy processability, and flexibility.^[1, 2] Polymer nanocomposites (PNCs) are a multiphase solid material in which one of the phases has dispersed in the other phase at a nanometer level. PNCs have attracted much interest in both academic and industrial fields for their unique physical, chemical and biological properties.^[3] Through control of the additives at the nanoscale level, PNCs are able to maximize property enhancement of selected polymer systems to meet the requirements of military, aerospace, and commercial applications or achieve even better performances. The introduction of inorganic or organic nanoparticles as additives into polymer systems has resulted in PNCs exhibiting multifunctional, high-performance polymer characteristics beyond what traditional filled polymeric materials possess. The properties of PNCs are determined not only by their individual components but also depend on their morphology and interfacial characteristics. In multifunctional PNCs, the reinforcements impart their special mechanical, optical, electrical, and magnetic properties to the composites. The polymer matrix holds the reinforcements and retains the properties of the polymers. The rapid research in PNCs has already developed various PNCs with multifunctionality showing substantial improvement in physicochemical properties.

1.1.1 Magnetic Polymer nanocomposites (MPNCs)

Magnetic polymer nanocomposites (MPNCs) have been extensively studied due to their wide technological applications, including electromagnetic interference (EMI) shielding,^[4] high density information storage,^[5] drug delivery,^[6] magnetic resonance imaging,^[7] bimodal imaging agent,^[8] and wastewater purification.^[9] Their magnetic properties have been considered to be

strongly associated with the particle morphology (size and shape) and crystalline structure. Qiu *et al.* have reported that the magnetic carbon nanoadsorbents derived from cellulose were fabricated through a calcination method by using the Fe_3O_4 nanoparticles (MC-O) and $\text{Fe}(\text{NO}_3)_3$ (MC-N) as the iron precursors retaining great hexavalent chromium (VI) removal performance.^[10] As Figure 1-1 shows, both MC-O and MC-N exhibit good magnetic properties. MC-O exhibits a saturation magnetization of $\sim 53 \text{ emu g}^{-1}$, whereas MC-N shows a larger saturation magnetization of $\sim 61 \text{ emu g}^{-1}$. A slightly decreased saturation magnetization was observed for both MC-O and MC-N after being treated with the Cr(VI) solutions of pH 7.0, whereas the magnetization decreased sharply after being treated with an initial pH of 1.0, especially for the MC-N. Both MC-O and MC-N (2.5 g L^{-1}) can remove 4.0 mg L^{-1} Cr(VI) within 10 min. The Cr(VI) removal by the magnetic carbons is highly dependent on the pH. MC-O and MC-N have the maximum adsorption capacities of 293.8 and 327.5 mg g^{-1} , respectively. MC-O has a better Cr(VI) removal rate and capacity than MC-N in neutral and basic solutions, whereas MC-N does better in acid solution. These nanoadsorbents could be easily separated from solution by using a permanent magnet after being treated with Cr(VI).

1.1.2 Electrically Conductive Polymer Nanocomposites

Among the PNCs, conductive PNCs are one of the most important materials. Generally, conductive PNCs can be divided into two categories. One is adding conductive nanofillers to the insulating polymer matrix, and another is to use the conductive polymer as the hosting matrix. Recently, conductive polymer composite (CPC) based strain sensors have attracted attention due to their quick response in the form of electrical resistance variation when subjected to tensile or compressive strain.^[11-14] Liu *et al.* have studied that graphene/ thermoplastic polyurethane (TPU)

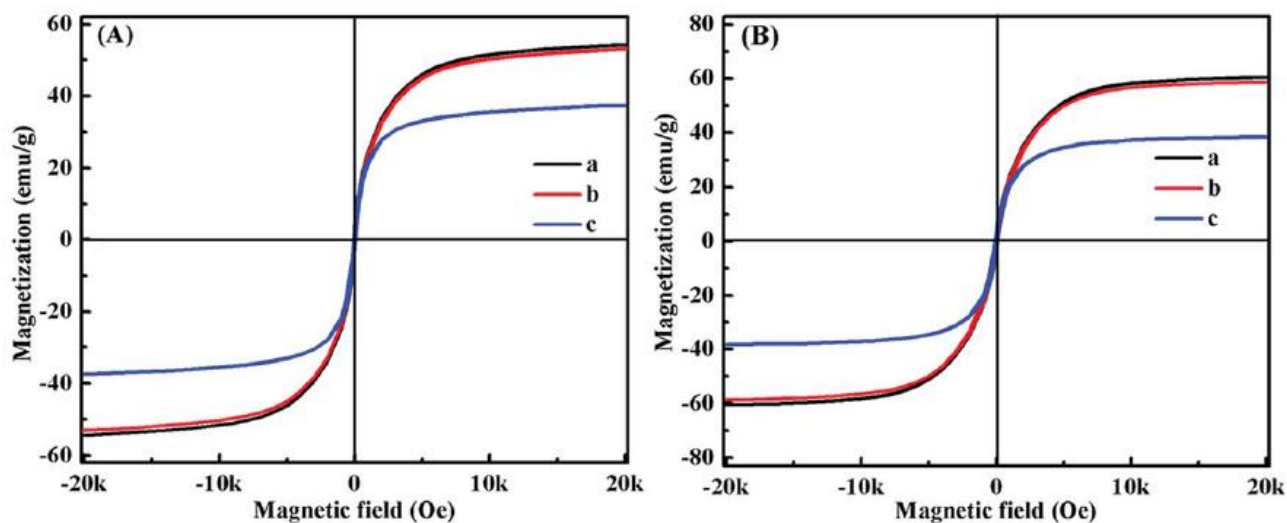


Figure 1-1. (A) Magnetic hysteresis loop of the MC–O (a) before and after being treated with Cr(VI) solution at pH (b) 7.0 and (c) 1.0; (B) magnetic hysteresis loop of MC–N (a) before and after being treated with Cr(VI) solution at pH (b) 7.0 and (c) 1.0.

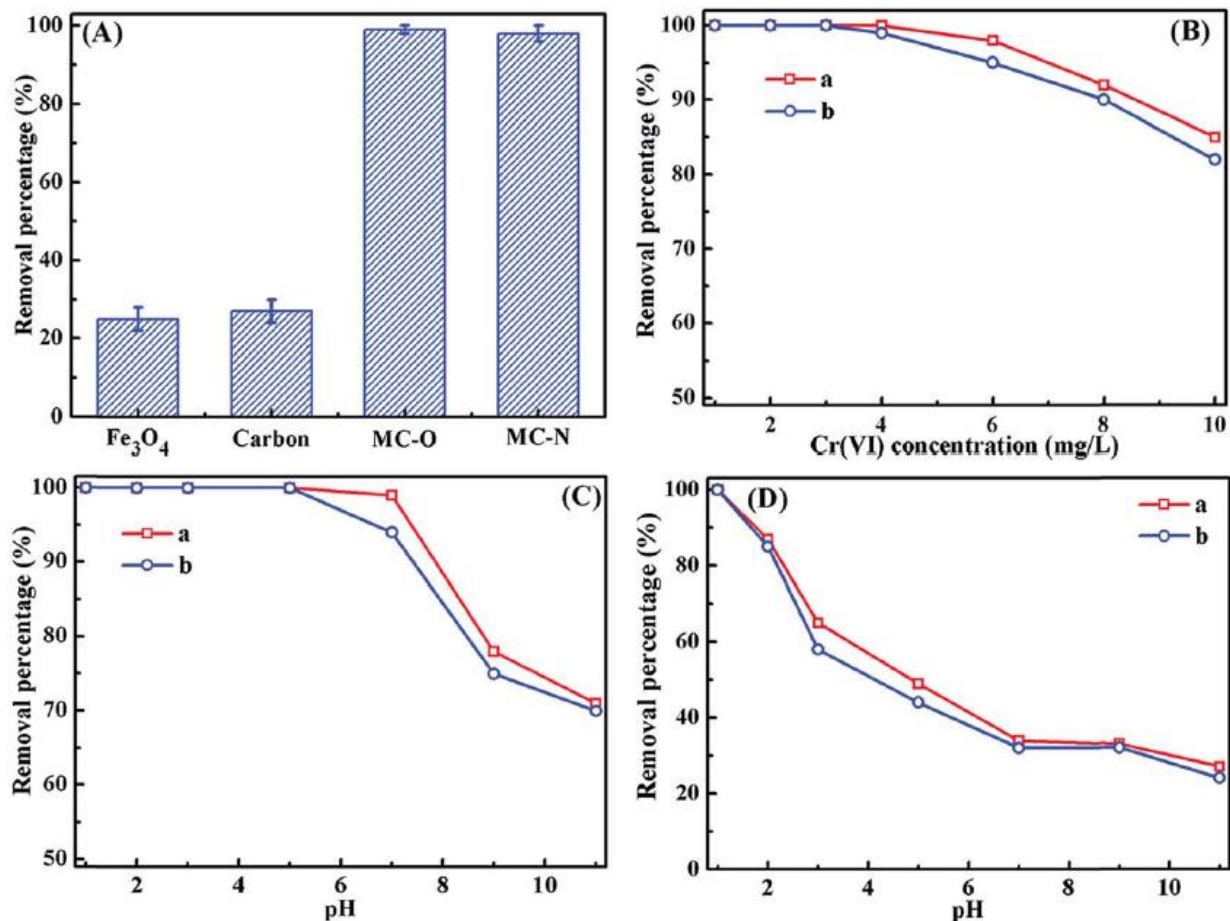


Figure 1-2. (A) Cr(VI) removal performance of different adsorbent (Cr(VI) concentrations: 4.0 mg L⁻¹, pH = 7.0, adsorbent dosage: 50.0 mg, volume: 20 mL, treating time: 10 min); (B) effect of initial Cr(VI) concentration on Cr(VI) removal performance (adsorbent dosage: 50.0 mg, volume: 20 mL, pH: 7.0, treating time: 10 min); and the effect of solution pH on the Cr(VI) removal performance by (a) MC-O and (b) MC-N with the initial Cr(VI) concentration of (C) 4.0 and (D) 1000 mg L⁻¹ (adsorbent dosage: 50.0 mg, volume: 20.0 mL, treating time: 10 min).

CPCs were prepared using the co-coagulation plus compression molding technique.^[15] The graphene sheets, which have a good H-bonding interaction with the TPU matrix, have been distributed in the TPU matrix homogeneously. The volume conductivity of CPCs is increased by about 8 orders of magnitude when the graphene loading is increased from 0.1 to 0.15 wt% as presented in Figure 1-3. Due to the good dispersion of graphene in the TPU matrix, an ultralow percolation threshold of 0.1 wt% was achieved. Figure 1-4a shows the relative resistance R/R_0 (R represents the resistance during cycle loading and R_0 is the original resistance of the sample) variation for the 1st cycle to 5% strain at a strain rate of 0.1 min^{-1} . The value of R/R_0 increases gradually with increasing strain, which is defined as the positive strain effect. During the cyclic loading, as shown in Fig. 1-4b&c, nanocomposites exhibiting different trends during the unloading process, good recoverability and reproducibility after stabilization by cyclic loading were obtained. In addition, about 100 cycles were conducted for TPU-0.2G, the strain sensing behavior still showed good recoverability and reproducibility until cycles 81–100, as shown in Figure 1-4d.

1.1.3 Flame-Retardant Polymer nanocomposites

Generally, two types of nanoparticles can be applied to enhance the flame retardancy of the polymer matrix. One is inorganic nanoparticles including alumina trihydrate,^[16] layered double hydroxides (LDHs),^[17] clay,^[18] and montmorillonite (MMT).^[19] However, the flame retardancy of the nanocomposites with inorganic nanoparticles largely depends on their dispersion quality. Because of the poor compatibility between organic and inorganic materials, additional surface modification^[20] or compatibilization^[21] is normally deployed to achieve good dispersion of silicate nanoparticles within the polymer matrix. The other type of additive is organic nanoparticles,

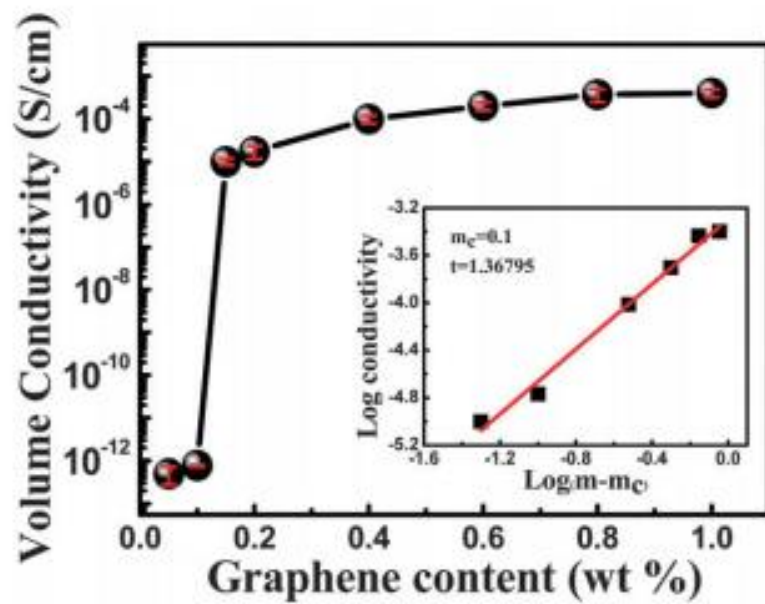


Figure 1-3. Volume conductivity as a function of graphene loading. The inset shows the log conductivity vs. log (m-m_c).

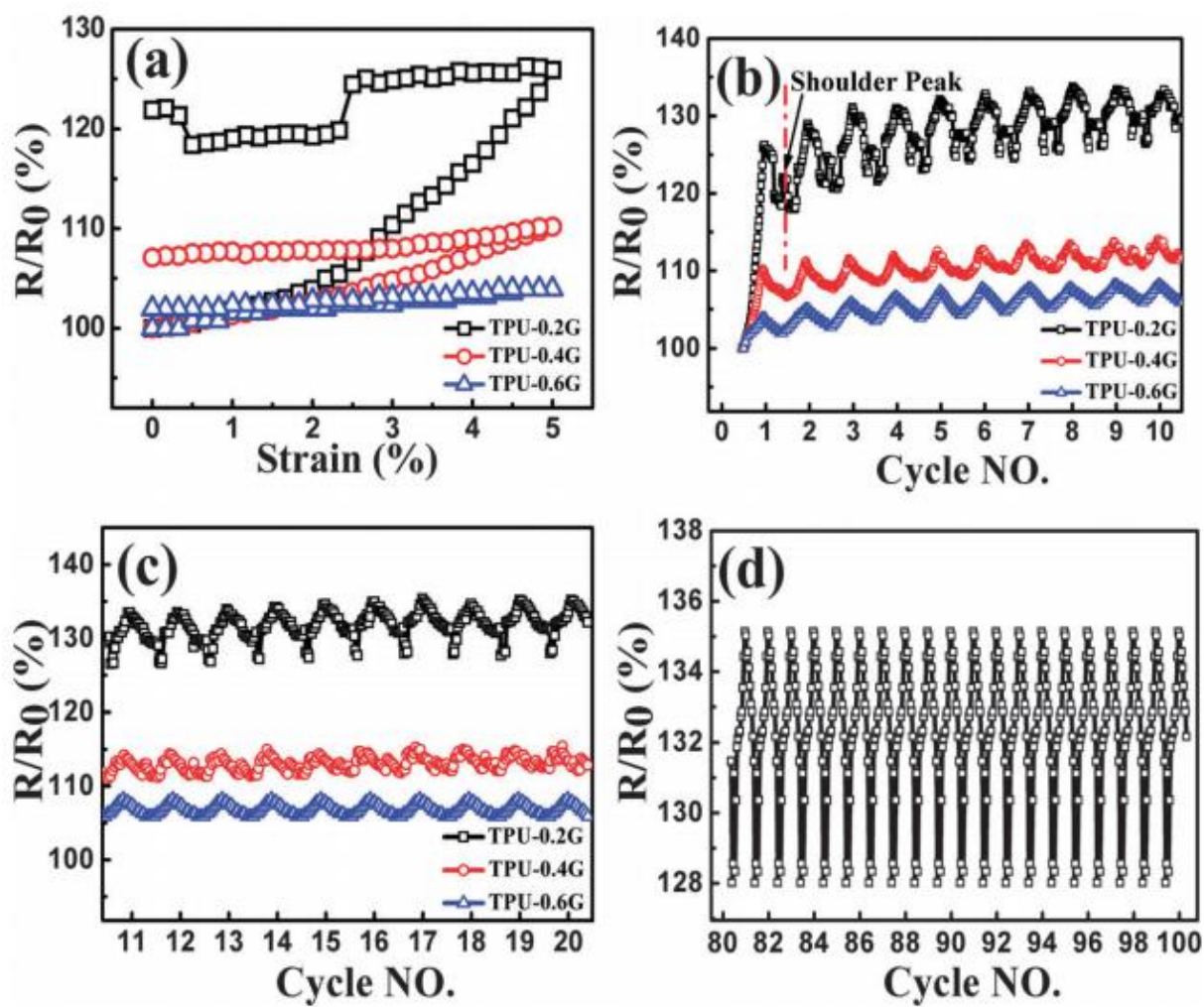


Figure 1-4. Resistance-strain behavior of composites with different graphene content, up to 5% strain at the strain rate of 0.1 min⁻¹, during the 1st cycle (a) and cyclic loading (b and c), (d) resistance-strain behavior of TPU-0.2G for cycles 81–100.

such as phosphorus-based^[22] and nitrogen-based flame retardants, including melamine and its derivatives.^[23] He *et al.* have investigated a facile ex situ solution-based mixing method, which was employed to prepare the PP/CNT PNCs. The surface of hydroxyl (OH) CNTs was modified with silane coupling agent-3-aminopropyltriethoxysilane (APTES) in order to introduce functional groups and maleic-anhydride-grafted polypropylene MAPP was used as a surfactant to further aid the dispersion of the functionalized CNTs within PP matrix.^[24] The flame retardancy of PP was improved by the combination of functional CNTs and MAPP-1, which is attributed to the better dispersion of functional CNTs and the introduced silicon-containing APTES, as revealed in Figure 1-5.

1.1.4 Electromagnetic Field Absorbing Polymer Nanocomposites

Embedding magnetic nano/microstructures into polymer matrix for electromagnetic (EM) wave absorption is one of the most effective approaches for electromagnetic interference (EMI) shielding.^[25] Theoretically, magnetic nanostructures, such as iron nanoparticles, can provide high absorption over a wide frequency range as a result of their high magnetization,^[26, 27] high Snoek's limit, and quantum size effect.^[28] Magnetic NPs are ideal to serve as EM absorbers because of their small size^[29] and large specific surface area,^[30] leading to an interface polarization^[31] and effective usage of active metals.^[32] However, high frequency (i.e., in GHz range) permeability of the metallic magnetic materials can be drastically decreased due to the ferromagnetic resonance^[33] and eddy-current losses (a source of energy loss in alternating current inductors, etc.) induced by the EM wave.^[34] The decreased permeability will significantly reduce the EM wave absorption efficiency in the GHz range. Another type of EM wave absorption material is polymer composites filled with carbon-based nanofillers.^[35-37] He *et al.* have fabricated PP MPNCs reinforced with either Fe@Fe₂O₃ core-shell NPs or MWNTs decorated with Fe@Fe₂O₃ core-shell NPs in the

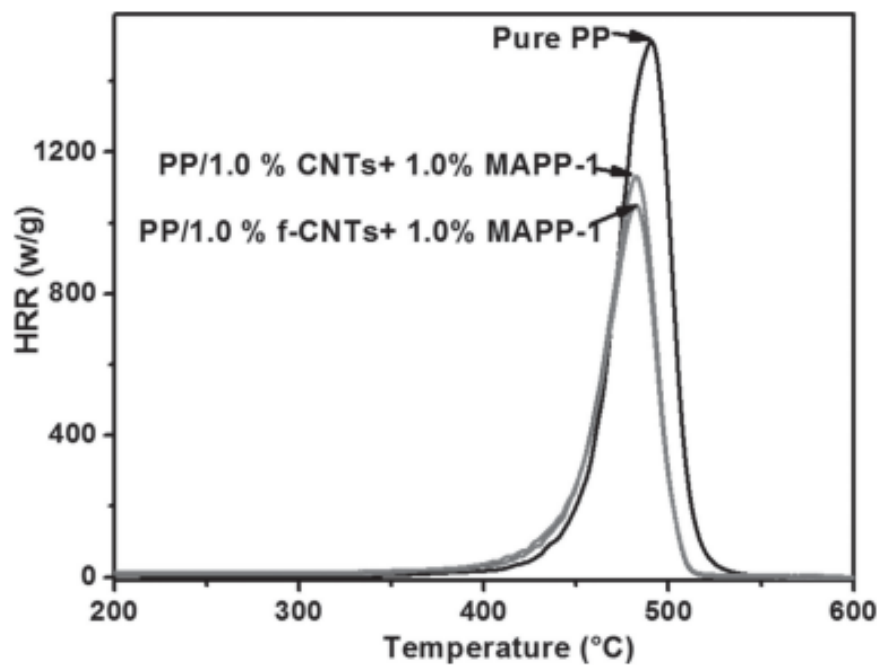


Figure 1-5. Heat release rate (HRR) curves as a function of temperature for PP, nanocomposites of PP/1% MAPP-1/CNTs, and nanocomposites of PP/1% MAPP-1/f-CNTs.

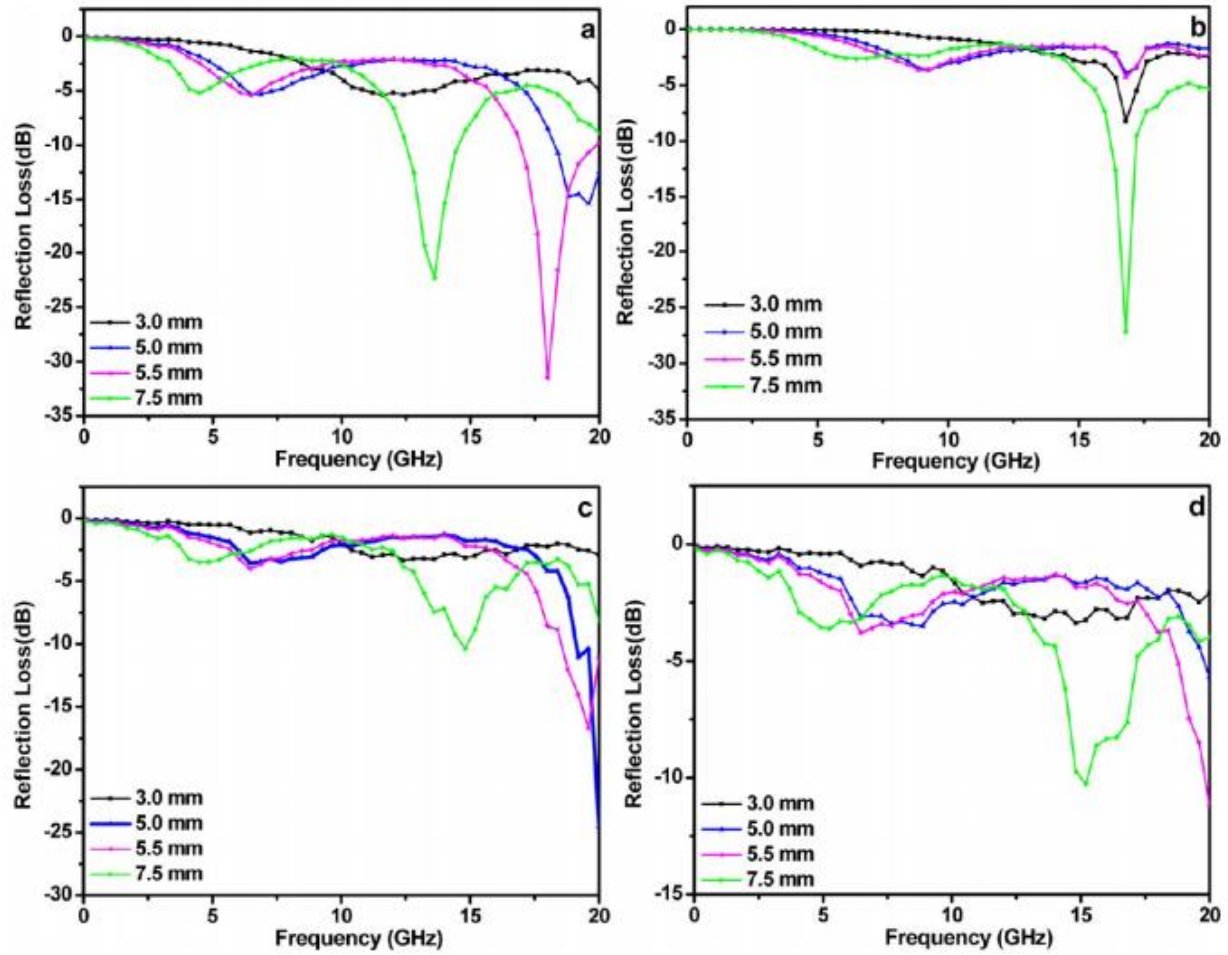


Figure 1-6. Reflection losses of (a) PP/5.0% PP-g-MA(S)/20.0% Fe, (b) PP/5.0% PP-g-MA(S)/1.0 MWNTs, (c) PP/5.0% PP-g-A(S)/1.0 MWNTs/20.0% Fe, and (d) PP/5.0% PP-g-MA(L)/1.0 MWNTs/20.0% Fe MPNCs.

presence of surfactant PP-g-MA, which is promising for high efficiency EM wave absorption application with controllable frequency range at the GHz level.^[4] A minimum -31.5 dB reflection losses (RL), corresponding to more than 99.9% of the EM wave, can be reached, and different reflection loss frequency ranges can be achieved by simply varying the absorber thickness, as estimated in Figure 1-6.

Multifunctional features attributable to polymer nanocomposites consist of improved thermal resistance, flame resistance, moisture resistance, decreased permeability, charge dissipation, and chemical resistance. Development of materials with multifunctionality, whether microscale or nanoscale, must simultaneously balance four interdependent aspects: constituent selection, processing, fabrication, and performance. The rapid development of PNCs has opened a new perspective for designing smart materials.

1.2. Preparation of Polymer Nanocomposites

Due to the different physical and chemical properties, different processing methods and conditions are needed for polymer systems to be fabricated. Polymer/inorganic nanocomposites can be prepared by in situ polymerization or by a blending processes, of which there are basically two types: solution blending and melt blending.^[38-40] With in situ polymerization, the nanofillers are dispersed in the monomers and polymerization occurs in the presence of initiators. In solution blending, the nanofillers are first dispersed in the solvent and then the polymer is dissolved. Finally, the above solution is stirred for the desired time and the solvent is removed at reduced pressure to produce the polymer composites. In contrast, with melt blending the nanofillers are added to a molten polymer. The distribution of the nanofiller is better with solution blending and in situ polymerization compared with melt blending; however, melt blending is regarded as a cost-effective, environmentally friendly, and industrially accepted method in comparison with the

others. In recent years, the surface coating method has been applied in preparation of multifunctional PNCs.^[41, 42]

1.3. Interface Engineered Nanostructures

It is a challenge to fabricate PNCs with good performance. The current research emphasis and theoretical work on PNCs is to find relationships between the effective properties of polymer composites (such as Young's modulus, tensile strength, and thermomechanical parameters) and the properties of constituents (polymer matrix and reinforcement), volume fraction of components, shape and arrangement of reinforcement, and matrix–reinforcement interaction. These results can help predict and control the properties of PNCs. Experimental results have revealed that the reinforcement size and morphology of polymer and reinforcement play a very important role in determining the performance of polymer nanocomposites. Also, the properties of polymer nanocomposites will depend on the nature of the dispersion and aggregation of the reinforcements. In a polymer composite, there exists an interphase with a layer of high-density polymer around the particle. The strength of the reinforcement–matrix interaction will affect the thickness and density of the interphase. The interface engineered nanostructures, including the inter-reinforcement distance and the arrangement of reinforcement, are important factors to be investigated. Generally, as their size decreases and number increases, the reinforcements become closer, and the bulk properties can be modified significantly. Due to the disparate physical and chemical systems developed by various different researchers, unique processing conditions are needed for different polymer systems to be formed.

1.4. Dissertation Overview

This dissertation is devoted to investigating the effects of the interface between nanofillers and polymers on the physiochemical properties of PNCs prepared by both solvent and novel microwave radiation methods. The rheological behavior, thermal stability, thermal conductivity, electrical conductivity and optical properties will be systematically studied.

In Chapter 2, we used a solvent extraction method to synthesize homogenous PNCs with magnetic properties to investigate the advantages and disadvantages of the PNCs with well-dispersed nanofillers. The thermogravimetric analyzer (TGA) and microscale combustion calorimetry (MCC) revealed an enhanced thermal stability and reduced flammability. Furthermore, the observed monotonically decreased complex viscosity indicated a strong shear thinning behavior in the PNCs.

Chapter 3 presents a discontinuous structure of gold nanoparticles (Au NPs) on the surface of a sub-micrometer sphere polymer with a layer of alternative polymer film. A surface interaction is exhibited between the polymer spheres and the Au NPs. The real permittivity of the PNCs is much higher than that of the pure polymer spheres, and an improved thermal stability is obtained in the PNCs. The PNCs also display a lower bandgap than that of pure polymer sphere.

Chapter 4 describes a study of CNTs coated on the surface of gelated/swollen soft Polypropylene (PP) powders that were easily pressed together and formed a network structure within the hosting materials, which led to outstanding electrical properties. The melt rheological behavior of the PNCs, including viscosity at steady state, viscosity storage, loss moduli, and loss factor were studied. For all PNCs, the thermal stability was tested by TGA. The effects of CNTs on the crystalline structure of PP including crystal structure, crystallization temperature, and

crystalline fraction, were evaluated. The effects of both the CNT loading and the processing temperature on the optical properties were studied by the Tauc plot and theoretically analyzed with the strain loaded on the CNTs in the PP matrix. The unique dielectric properties of the PNCs were theoretically analyzed with the popular Drude model, and interband transition phenomenon for the permittivity transitions between positive and negative.

In Chapter 5, we utilized the same method as that in Chapter 4 to study the effects of CNTs on different polymer matrices. The effects of CNTs loading level and processing temperature on the electrical conductivity, optical property, and thermal conductivity were investigated. The room temperature resistance variation as a function of magnetic field (M-R) was recorded. The electron transport mechanism was investigated by the variable range hopping approach. Both positive and negative magnetoresistance were analyzed by using a wave function shrinkage model and a forward interference model, respectively.

Chapter 6 presents highly electrically conductive PP/CNT PNCs were successfully synthesized by an efficient microwave solvent-free irradiation method under an inert atmosphere and controlled treating time. The formation of CNTs on the surface of PP granules depends on the microwave heating time, and the final electrical conductivity is related to the different processing temperatures. This solvent-free preparation procedure was extremely mild, easy to control, and repeatable. The morphology of the PNCs was investigated by SEM. The influences of the CNTs on the EOCs were studied by XRD and DSC. The thermal stability of PNCs was examined by TGA. The rheological behavior of the PNCs, including storage and loss moduli, loss factor, and viscosity were investigated. For all the PNCs, the effects of CNT loading level and processing temperature on the electrical conductivity, optical properties, and magnetoresistance were

investigated. The electrical conductivity mechanism was theoretically analyzed by the variable range hopping approach.

A summary of this dissertation research and future work are provided in Chapter 7.

1.5. References

- [1] L. S. Schadler, "*Polymer - Based and Polymer - Filled Nanocomposites*", Wiley Online Library, 2003.
- [2] J. H. Koo, "*Polymer nanocomposites*", McGraw-Hill Professional Pub., 2006.
- [3] H. Fischer, *Materials Science and Engineering: C* **2003**, 23, 763.
- [4] Q. He, T. Yuan, X. Zhang, X. Yan, J. Guo, D. Ding, M. A. Khan, D. P. Young, A. Khasanov, Z. Luo, *The Journal of Physical Chemistry C* **2014**, 118, 24784.
- [5] H. Goesmann, C. Feldmann, *Angewandte Chemie International Edition* **2010**, 49, 1362.
- [6] T. Hoare, B. P. Timko, J. Santamaria, G. F. Goya, S. Irusta, S. Lau, C. F. Stefanescu, D. Lin, R. Langer, D. S. Kohane, *Nano letters* **2011**, 11, 1395.
- [7] L. Cheng, K. Yang, Y. Li, J. Chen, C. Wang, M. Shao, S. T. Lee, Z. Liu, *Angewandte Chemie* **2011**, 123, 7523.
- [8] P. Howes, M. Green, A. Bowers, D. Parker, G. Varma, M. Kallumadil, M. Hughes, A. Warley, A. Brain, R. Botnar, *Journal of the American Chemical Society* **2010**, 132, 9833.
- [9] J. Zhu, H. Gu, S. B. Rapole, Z. Luo, S. Pallavkar, N. Haldolaarachchige, T. J. Benson, T. C. Ho, J. Hopper, D. P. Young, *RSC Advances* **2012**, 2, 4844.
- [10] B. Qiu, H. Gu, X. Yan, J. Guo, Y. Wang, D. Sun, Q. Wang, M. Khan, X. Zhang, B. L. Weeks, *Journal of Materials Chemistry A* **2014**, 2, 17454.
- [11] L. Lin, S. Liu, Q. Zhang, X. Li, M. Ji, H. Deng, Q. Fu, *ACS applied materials & interfaces* **2013**, 5, 5815.
- [12] J. Zhu, S. Wei, J. Ryu, Z. Guo, *The Journal of Physical Chemistry C* **2011**, 115, 13215.
- [13] H. Liu, J. Gao, W. Huang, K. Dai, G. Zheng, C. Liu, C. Shen, J. Guo, X. Yan, Z. Guo, *Nanoscale* **2016**, 8, 12977.
- [14] Q. He, T. Yuan, X. Zhang, S. Guo, J. Liu, J. Liu, X. Liu, L. Sun, S. Wei, Z. Guo, *Materials Research Express* **2014**, 1, 035029.
- [15] Y. Lan, H. Liu, X. Cao, S. Zhao, K. Dai, X. Yan, G. Zheng, C. Liu, C. Shen, Z. Guo, *Polymer* **2016**, 97, 11.
- [16] X. Zhang, F. Guo, J. Chen, G. Wang, H. Liu, *Polymer Degradation and Stability* **2005**, 87, 411.
- [17] W. Chen, B. Qu, *Chemistry of Materials* **2003**, 15, 3208.
- [18] S. Zhang, A. R. Horrocks, R. Hull, B. K. Kandola, *Polymer Degradation and Stability* **2006**, 91, 719.
- [19] Y. Hu, S. Wang, Z. Ling, Y. Zhuang, Z. Chen, W. Fan, *Macromolecular Materials and Engineering* **2003**, 288, 272.
- [20] Q. Sun, F. J. Schork, Y. Deng, *Composites Science and Technology* **2007**, 67, 1823.
- [21] W. Lertwimolnun, B. Vergnes, *Polymer* **2005**, 46, 3462.
- [22] S.-Y. Lu, I. Hamerton, *Progress in Polymer Science* **2002**, 27, 1661.
- [23] H. Horacek, R. Grabner, *Polymer Degradation and Stability* **1996**, 54, 205.
- [24] Q. He, T. Yuan, X. Yan, D. Ding, Q. Wang, Z. Luo, T. D. Shen, S. Wei, D. Cao, Z. Guo, *Macromolecular Chemistry and Physics* **2014**, 215, 327.
- [25] J. van Wonerghem, S. Mørup, S. W. Charles, S. Wells, J. Villadsen, *Physical review letters* **1985**, 55, 410.
- [26] G. S. Chaubey, C. Barcena, N. Poudyal, C. Rong, J. Gao, S. Sun, J. P. Liu, *Journal of the American Chemical Society* **2007**, 129, 7214.

- [27] F. Rahman, K. H. Langford, M. D. Scrimshaw, J. N. Lester, *Science of the Total Environment* **2001**, 275, 1.
- [28] D. L. Leslie-Pelecky, R. D. Rieke, *Chemistry of materials* **1996**, 8, 1770.
- [29] P. Tartaj, M. del Puerto Morales, S. Veintemillas-Verdaguer, T. González-Carreño, C. J. Serna, *Journal of Physics D: Applied Physics* **2003**, 36, R182.
- [30] R. M. Crooks, M. Zhao, L. Sun, V. Chechik, L. K. Yeung, *Accounts of chemical research* **2001**, 34, 181.
- [31] J. Zhang, S. Xu, E. Kumacheva, *Journal of the American Chemical Society* **2004**, 126, 7908.
- [32] R. Ferrando, J. Jellinek, R. L. Johnston, *Chemical reviews* **2008**, 108, 845.
- [33] P. Singh, V. Babbar, A. Razdan, S. Srivastava, T. Goel, *Materials Science and Engineering: B* **2000**, 78, 70.
- [34] J. Zhu, S. Wei, N. Haldolaarachchige, D. P. Young, Z. Guo, *The Journal of Physical Chemistry C* **2011**, 115, 15304.
- [35] J.-M. Thomassin, C. Pagnoulle, L. Bednarz, I. Huynen, R. Jerome, C. Detrembleur, *Journal of Materials Chemistry* **2008**, 18, 792.
- [36] J. Ling, W. Zhai, W. Feng, B. Shen, J. Zhang, W. g. Zheng, *ACS applied materials & interfaces* **2013**, 5, 2677.
- [37] Z. Chen, C. Xu, C. Ma, W. Ren, H. M. Cheng, *Advanced materials* **2013**, 25, 1296.
- [38] S. S. Ray, M. Okamoto, *Progress in polymer science* **2003**, 28, 1539.
- [39] F. Hussain, M. Hojjati, M. Okamoto, R. E. Gorga, *Journal of composite materials* **2006**, 40, 1511.
- [40] T. Kuilla, S. Bhadra, D. Yao, N. H. Kim, S. Bose, J. H. Lee, *Progress in polymer science* **2010**, 35, 1350.
- [41] X. Yan, M. Li, J. Long, X. Zhang, H. Wei, Q. He, D. Rutman, D. Cao, S. Wei, G. Chen, *Macromolecular Chemistry and Physics* **2014**, 215, 1098.
- [42] X. Zhang, X. Yan, Q. He, H. Wei, J. Long, J. Guo, H. Gu, J. Yu, J. Liu, D. Ding, *ACS applied materials & interfaces* **2015**, 7, 6125.

Chapter 2. Traditional Uniform Dispersion of Nanoparticles in a Polymer Matrix

Abstract

Polystyrene (PS)/magnetite (Fe_3O_4) polymer nanocomposites (PNCs) were successfully synthesized by a solvent extraction method. The scanning electron microscope (SEM) revealed that the NPs were well distributed in the PS matrix with 5, 10 and 20 wt% without obvious agglomeration. The thermogravimetric analysis (TGA) and microscale combustion calorimeter (MCC) revealed an enhanced thermal stability and reduced flammability. The differential scanning calorimetry (DSC) demonstrated that both the glass transition temperature (T_g) and the melting temperature (T_m) increased with increasing the Fe_3O_4 NPs loading. The observed monotonically decreasing complex viscosity indicated a strong shear thinning behavior in the PNCs; meanwhile, the percolation took place at low frequency range (0.1-1 Hz) when the NPs were introduced into the matrix. The T_g of the PS/ Fe_3O_4 nanocomposites determined from the dynamic mechanical analysis (DMA) shifted to a higher temperature compared with that of pure PS. Enhanced dielectric properties were related to the Fe_3O_4 nanoparticle loadings. In addition, the PS/ Fe_3O_4 PNCs exhibited superparamagnetic behavior at room temperature.

2.1. Introduction

Magnetic polymer nanocomposites (PNCs) have captured intense attention owing to their unique physicochemical properties and manifold potential applications including energy storage devices,^[1] magnetic sensors,^[2] fire retardants,^[3] microwave absorbers^[4,5] and magnetic recording information.^[6] Magnetic properties can be obtained by either physical or chemical methods, such as surface initiated polymerization,^[7] in-situ polymerization,^[8] solution blending,^[9,10] melt blending,^[11] layer-by-layer deposition^[12] and surface wetting method,^[13] to incorporate magnetic nanoparticles (NPs) including iron,^[14] cobalt,^[15] nickel^[16] and their alloys in the non-magnetic polymer matrix. Magnetic NPs can not only introduce the magnetization but also improve the thermal stability,^[17] mechanical properties,^[18] optical properties,^[19] combustion properties^[3] and dielectric properties^[20] through combining the merits of the organic polymer matrix and the inorganic components with different nano-structures and sizes. Compared with other magnetic NPs, magnetite nanoparticles (Fe_3O_4) are considered as one of the most promising materials due to the fairly large magnetization and admirable conductive properties.^[21]

Polystyrene (PS) is one of the most important polymers of today. Its popularity stems from the fact that it possesses many unique properties, such as good processability, rigidity, transparency, low water absorbability, and that it can be produced at low cost. Therefore, there are several studies in the literature about PS with Fe_3O_4 NPs. Huang et al.^[22] have prepared core-shell structure particles comprising nearly monodisperse PS spheres as cores and Fe_3O_4 as shells. By using slow injection, the thickness of the shell was controlled in the range of 0-60 nm. After studying the composite and the structure of the shell, it was found that there are some differences between the magnetic composite spheres shelled with Fe_3O_4 and pure Fe_3O_4 particles, such as the size of the magnetite and the ferromagnetic properties. Meanwhile, the spheres exhibited

superparamagnetic characteristics when the thickness of the Fe_3O_4 shell was less than 15 nm. Zhao et al.^[23] have prepared PS/ Fe_3O_4 composite microspheres by an emulsion polymerization method. The modified Fe_3O_4 nanoparticles were copolymerized with styrene and acrylic acid to form the magnetic polymer microspheres with carboxyl groups to study the preparation of the nanosized, mono-disperse, cross-linked, magnetic composite polymer micro-spheres. Zhong et al.^[24] have investigated the PS/ Fe_3O_4 composites synthesized by a facile in situ bulk radical polymerization. Shi et al.^[25] reported polyethylene-oxide-modified PS/ Fe_3O_4 nanospheres synthesized by the miniemulsion/emulsion polymerization with quantum dots (QDs) as a second nanofiller. The QDs, immobilized on the surfaces of magnetic Fe_3O_4 composite nanospheres, exhibited intense visible-light emission in the fluorescence spectroscopy. Meanwhile, the Fe_3O_4 NPs respond to an external magnetic field by increasing the temperature of the surrounding environment, which can be used therapeutically. Although the morphology, superparamagnetic properties and thermal stability of the fabricated PS/ Fe_3O_4 PNCs have been reported, the dielectric permittivity, melt rheological behavior, flammability, and thermo-mechanical properties of the PS/ Fe_3O_4 PNCs fabricated using solvent extraction method have not been reported.

In this work, the PS/ Fe_3O_4 nanocomposites with various Fe_3O_4 particle loadings were prepared by a facile solvent extraction method. The scanning electron microscope (SEM) was used to characterize the dispersion quality of Fe_3O_4 NPs and the morphology of the PS/ Fe_3O_4 nanocomposites. The effects of the Fe_3O_4 NPs on the crystallization behavior of PS were also studied by X-ray diffraction (XRD) and differential scanning calorimetry (DSC). The thermal stability of the PS/ Fe_3O_4 nanocomposites was tested by thermogravimetric analysis (TGA). The effects of the particle loading on the storage/loss modulus of the PS/ Fe_3O_4 nanocomposites were

studied systematically. The thermo-mechanical, magnetic, dielectric, and flammability properties were also studied and discussed.

2.2. Experimental

2.2.1 Materials

Polystyrene (PS) (melt flow rate = 9.0, $\overline{M}_n = 83900$, $\overline{M}_w = 225600$) was supplied by Total Petrochemicals USA, Inc. Anhydrous *N,N*-dimethylformamide (DMF, 99.9%) was purchased from Alfa Aesar. The Fe₃O₄ NPs were provided by Nanjing Emperor Nano Material Co., Ltd., China. All the materials were used as received without any further treatment.

2.2.2 Preparation of Fe₃O₄/PS Nanocomposites

The PS/DMF solutions were prepared by magnetic stirring at room temperature with a polymer loading of 30 wt % until the PS was completely dissolved. Different loadings of Fe₃O₄ NPs (5, 10 and 20 wt % with regard to the weight of PS and NPs) were then added to the PS/DMF solutions. After completely wetting the NPs with the polymer solution, both mechanical stirring (400 rpm, 90 min) and ultrasonication (90 min) were subsequently performed to disperse the NPs in the PS solution. The nanoparticle suspended solutions were then transferred to deionized water to immobilize the Fe₃O₄ NPs in the PS matrix. The PNCs were precipitated immediately from the DI water by using a solvent extraction process. After that the PNCs were dried in a vacuum oven at 60 °C for 48 hours to eliminate the residue DMF and DI water. Pure PS was also prepared from the same procedures without adding the Fe₃O₄ NPs.

2.2.3 Characterization

The morphologies of pure PS and its Fe₃O₄ nanocomposites were characterized using a Helios NanoLab 400 DualBeam scanning electron microscope (SEM). The SEM specimens were coated with a thin gold for better imaging. The crystalline structure of pure PS and its PNCs was

studied by X-ray diffraction (XRD), which was carried out by a Bruker AXS D8 Discover diffractometer operating with a Cu K α radiation source. The X-ray was generated at 40 kV and 27 mA power and XRD scans were recorded at 2 θ from 5 to 80° ($\lambda=0.154\text{nm}$). The thermal stability of pure PS and its Fe₃O₄ nanocomposites was investigated by thermogravimetric analysis (TGA, TA-Q500 instrument). The heating rate was 10 °C·min⁻¹, and the experiments were performed in a continuous air flow at a flow rate of 20 mL·min⁻¹. The temperature was ranged from 25 to 700 °C. The effects of the NPs on the thermal properties of PS were determined by using differential scanning calorimetry (DSC, TA-Q2000 instrument). Heating scans were performed at a rate of 10 °C·min⁻¹ in a continuous nitrogen flow rate of 50 mL·min⁻¹. Samples were sealed in a standard aluminum pan and the measurements were taken between 25-250 °C. The weight of each sample was approximately 10 mg. The DSC heat flow and temperature values were calibrated with an indium standard.

A Govmark MCC-2 microscale combustion calorimetry (MCC) was utilized to test the flammability of PS nanocomposites according to ASTM D7309-2007 (Method A). In a typical measurement, about 3mg of the sample was heated from 80 to 650 °C using a linear heating rate of 1 °C/s in a stream of nitrogen flow rate of 80 mL/min. The thermal degradation products of the sample in nitrogen were mixed with a 20 mL/min stream of oxygen prior to entering the 900°C combustion furnace to complete the nonflaming combustion. The rate and amount of heat were measured by MCC using an oxygen consumption calorimeter, which was produced by a complete combustion of fuel gases generated during the controlled pyrolysis of a milligram size specimen.

Dynamic mechanical analyses (DMA) were studied by using the TA Instruments AR 2000ex instrument in the torsion rectangular mode with a strain of 0.4% and a frequency of 1 Hz. The temperature range was from 30 to 140 °C. The melt rheological behavior of neat PS and its

PNCs were investigated using a TA Instruments AR 2000ex Rheometer. The frequency sweep was from 100 to 0.1 Hz. An environmental test chamber (ETC) and a steel parallel-plate geometry was used to perform the measurements at 230 °C in the linear viscoelastic (LVE) range with 1% strain under air atmosphere.

The magnetic properties were examined using in a 9 Tesla Physical Properties Measurement System (PPMS) by Quantum Design at room temperature. Agilent E4980A Precision LCR Meter (20 Hz to 2 MHz) with a signal voltage range of 0-2.0 V_{rms} and signal current range of 0-20.0 mA_{rms} was used to collect the dielectric data at room temperature. The samples used were 25 mm in diameter with ca. 2 mm thickness prepared from hot press machine at 190 °C. The frequency was ranged from 500 Hz to 2 MHz.

2.3. Results and Discussion

2.3.1 Morphology

The nanofiller size and the morphology play a very important role in determining the performance of the PNCs. Meanwhile, the properties of PNCs depend on the level of dispersion quality of the nanofillers. The morphological characterization is the most direct way to evaluate the level of the nanofiller dispersion. Figure 2-1 shows the SEM images of the cross-sectional surface of pure PS and the PNCs with a particle loadings of (a) 5, (b) 10 and (c) 20 wt%, respectively. The NPs were observed to be well dispersed in the PS matrix with 5, 10 and 20 wt% without obvious agglomeration of Fe₃O₄ NPs.

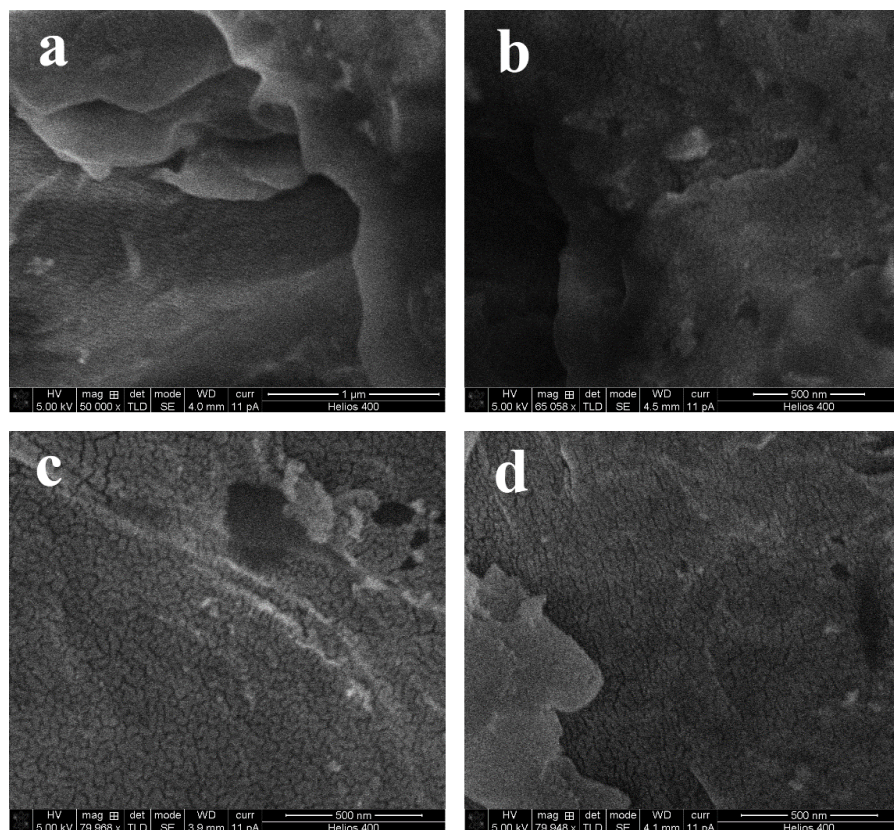


Figure 2-1. SEM images of the PNCs with a particle loading of (a) 5, (b) 10 and (c) 20 wt%, respectively.

2.3.2 X-ray Diffraction

Figure 2-2 shows the X-ray diffraction (XRD) patterns of the neat PS and PS/Fe₃O₄ PNCs with different weight percentages. The diffraction peaks at $2\theta = 30.2, 35.6$ and 57.2° , correspond to (220), (311) and (511) crystallographic planes of the crystalline Fe₃O₄ content.^[26,27] According to the Scherrer Equation (1), the average crystallite size can be estimated from the XRD pattern,^[28]

$$L = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where L is the average crystallite size, k is the shape factor, λ is the wavelength ($\lambda=0.154$ nm), β is the full width at half maximum, and θ is the angle at maximum intensity. The value of k depends on several factors, including the Miller index of the reflection plane and the shape of the crystal, which is normally 0.89 if the shape is unknown. Here, the peak of the PS/Fe₃O₄ NPs with a particle loading of 10 wt% at $2\theta = 35.6^\circ$ was chosen to calculate the crystallite size, and the average crystallite size of the Fe₃O₄ NPs is about 13.59 nm. The intensity of these diffraction peaks of the Fe₃O₄ NPs becomes stronger with increasing the nanoparticle loadings. A hump at 9.8° and a wide peak at 19° are characteristic of crystalline PS, as obtained in Figure 2-2, which shows a reduced intensity.^[29,30] This indicates a strong interaction between PS backbone and Fe₃O₄ NPs, as confirmed by the following FT-IR spectrum analysis. According to all the results, Fe₃O₄ NPs have a positive influence on the crystallites of PS.

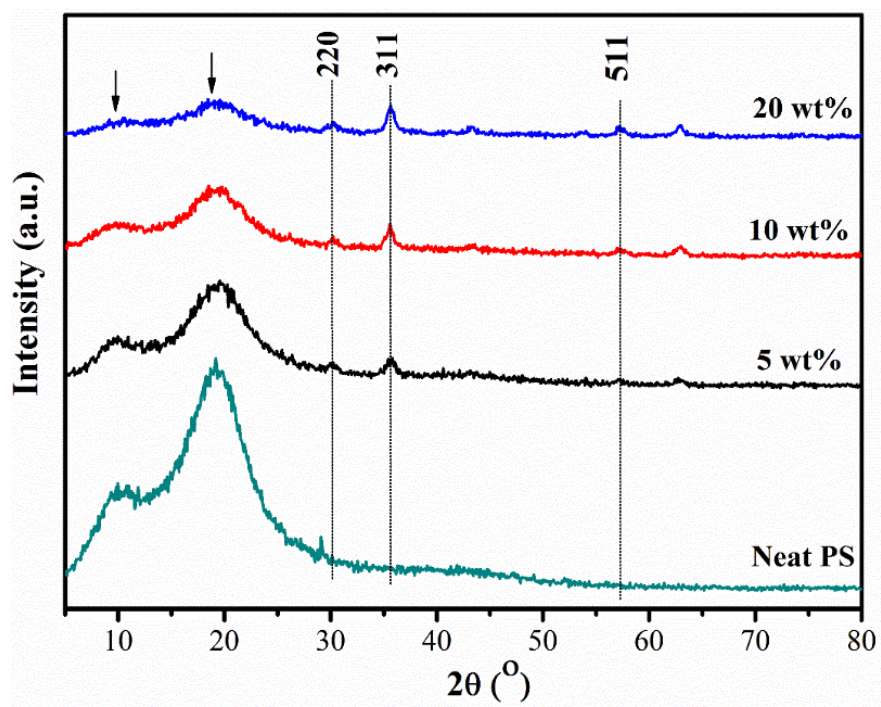


Figure 2-2. XRD patterns of pure PS and PS/ Fe_3O_4 nanocomposit

2.3.3 Thermal Stability

Figure 2-3(A) shows the TGA weight loss curves of neat PS and PS/ Fe_3O_4 PNCs, and Figure 2-3(B) shows the corresponding derivative weight loss curves. The normalized sample mass is slightly less than 100% after 260 °C, which is attributed to the elimination of moisture in the samples. The major weight loss of all the samples from 260-430 °C is due to a large scale thermal degradation of the PS chains.^[26,27,33] The Fe_3O_4 sample is also slightly less than 100% due to the loss of moisture and impurities. The weight residues of the PNCs with an initial nanoparticle loading of 5.0, 10.0 and 20.0 wt% are 4.5, 9.8 and 17.5%, respectively. The loading noticeably increased, and the corresponding temperature of the maximum rate of the weight loss increased as well, which are shown in the insert in Figure 2-3(B). As the Fe_3O_4 loading increases, the decomposition temperature is correspondingly increased in the PS/ Fe_3O_4 PNCs.

The onset degradation temperatures (T_{on}), the 10% mass loss temperature ($T_{10\%}$) and the temperatures of the maximum weight loss rate (inflection point, T_{max}) are summarized in Table 2-1. The results indicate that the Fe_3O_4 nanoparticle loading is not proportional to the onset degradation temperature. For example, the degradation temperature of the PNCs with a 10 wt% Fe_3O_4 nanoparticle loading is 12 °C higher than that of the PNCs at 5 wt% Fe_3O_4 nanoparticle loading and is increased by 6 °C from 10 to 20 wt%, but by only 3 °C from pure PS to the PNCs with a 5 wt% particle loading. The temperature of onset degradation (T_{on}), temperature of 10% mass loss ($T_{10\%}$), and the inflection point (T_{max}) are observed to increase with increasing the Fe_3O_4 NPs loading, listed in Table 2-1, which shows that the presence of Fe_3O_4 NPs stabilizes PS. The

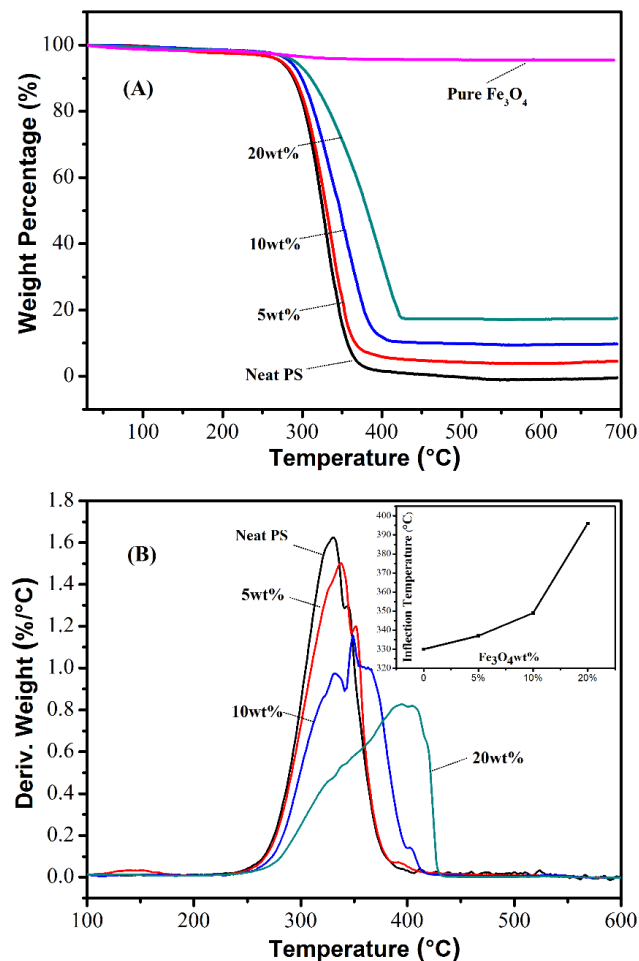


Figure 2-3. (A) TGA weight loss curves and (B) derivative weight loss curves of pure PS, Fe_3O_4 and PS/ Fe_3O_4 PNCs. Insert: the inflection point as a function of the loading of Fe_3O_4 NPs.

Table 2-1. TGA data of the pure PS and PS/ Fe_3O_4 nanocomposites.

Fe_3O_4 loading (wt%)	Neat PS	5 wt%	10 wt%	20wt%
T_{on} [°C]	272	275	287	293
$T_{10\%}$ [°C]	289	292	299	311
T_{max} [°C]	330	337	349	396

enhanced thermal stability in the PNCs has been reported in the other systems as well.^[34-37] The enhanced thermal stability of the PS/Fe₃O₄ PNCs results from the interaction between the PS matrix and the Fe₃O₄ NPs. The surface of the Fe₃O₄ NPs absorbs the free radicals produced in the decomposition of PS and restricts the mobility of the polymer molecules, which retards the degradation of the PS/Fe₃O₄ PNCs.^[38,39]

2.3.4 DSC Analysis

Figure 2-4 shows the DSC thermograms of PS nanocomposites with different Fe₃O₄ nanoparticle loadings, based on which the effects of the incorporated Fe₃O₄ NPs on the PS matrix can be explored from the aspects of both glass transition temperature (T_g) and melting temperature (T_m). The addition of Fe₃O₄ NPs in the PS matrix is observed to have a marginal effect on the T_g of PS and slightly increase T_m compared to that of neat PS, as seen in Figure 2-4. In addition, Uthirakumar et al have reported an improved T_g in the PS nanocomposites filled with montmorillonite.^[40] Both the confined polymer chains between the layers of fillers and the restricted segmental motions at the organic-inorganic interface are responsible for the increased T_g .^[40]

With a Fe₃O₄ nanoparticle loading of 10 and 20 wt%, the melting temperatures of the PNCs are around 2 and 3 °C higher than that (152 °C) of the pristine PS, respectively. The result of this phenomenon is the retarded mobility of the PS chains surrounded by Fe₃O₄ NPs, and a subsequently higher temperature is needed to move the long polymer chains.^[10] Noticeably, an increase in the Fe₃O₄ loading leads to wider and shallower exothermic curves, which indicate that the dispersed Fe₃O₄ NPs act as barriers to the formation of large PS crystallites.^[41]

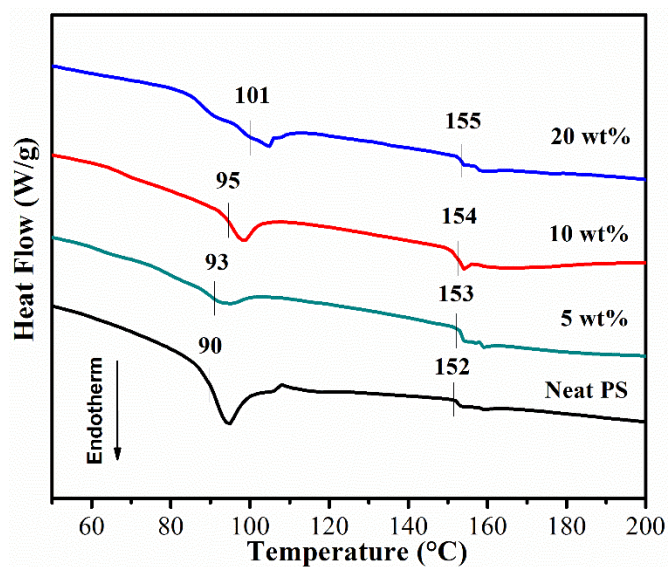


Figure 2-4. DSC thermograms of pure PS and PS/ Fe_3O_4 nanocomposites with different Fe_3O_4 nanoparticle loadings.

2.3.5 Flammability Properties

Microscale combustion calorimetry (MCC) was further utilized to evaluate the flammability of PS and its PNCs with different particle loadings by studying the heat release rate (HRR) as a function of temperature (Figure 2-5) and the heat release capacity (HRC), peak heat release rate (PHRR), total heat release (THR) and maximum pyrolysis rate (T_{PHRR}) are summarized in Table 2-2. HRR is the most important variable to assess the flammability and fire hazard of materials.^[42] Meanwhile, a relatively good indicator of the heat release rate is the heat release capacity HRC in the propensity for ignition and flaming combustion; a low value of HRC means low full fire hazard and low flammability.^[43] PHRR is the maximum HRR when one sample generates the highest rate of heat release. Compared with that of pure PS, the PHRR value of the PNCs with 20 wt% NPs loading is decreased by 16.28%. The HRC of the PS/Fe₃O₄ PNCs has a similar trend as PHRR (Table 2-2) which can be attributed to the existence of Fe₃O₄ nanoparticles. In addition, the total heat release THR and maximum pyrolysis rate (T_{PHRR}) decrease with increasing the particle loading. These are due to a higher initial thermal stability of pure Fe₃O₄ than that of pure PS shown in the TGA results, which can also explain the phenomenon that the temperature corresponding to PHRR increases with increasing the Fe₃O₄ nanoparticles loading. Apparently, the Fe₃O₄ nanoparticles (as metal components) can favor the char formation in the organic materials by reducing the reactive radical during depolymerization process.^[44] In addition, the formed char on the surface of materials can prevent the polymeric material from fast decomposition by obstructing heat being transferred from the heat source to the inner material,^[22] which further suggests that the Fe₃O₄ nanoparticles play a positive role in reduced flammability in the PS matrix.

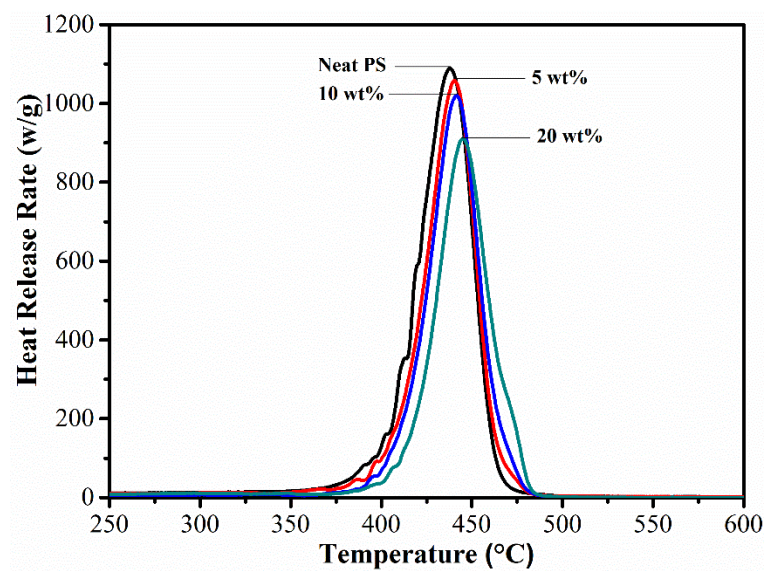


Figure 2-5. The HRR curves of PS/ Fe_3O_4 nanocomposites with a particle loading of 5, 10 and 20 wt%, respectively.

Table 2-2. MCC data of pure PS and PS/ Fe_3O_4 nanocomposites.

Samples	HRC (J/g K)	PHRR(w/g)	THR (kJ/g)	T_{PHRR} (°C)
Neat PS	1010	1081	38.4	437.8
5 wt%	988	1049	35.1	440.3
10 wt%	958	1016	34.2	441.7
20 wt%	847	905	31.7	445.1

2.3.6 Thermo-mechanical Properties

Dynamic mechanical analysis (DMA) was used to characterize the viscoelastic properties of the materials by providing specific information on the storage modulus (E'), loss modulus (E'') and $\tan\delta$ within the investigated temperature range.^[45] The E' reflects the elastic modulus of the nanocomposites; meanwhile, the E'' is related to the energy dissipation associated with the motion of polymer chains due to friction.^[17,46] The variation of E' of neat PS and PS/ Fe_3O_4 nanocomposites as functions of temperature is presented in Figure 2-6. Compared to neat PS, E' for the PS/ Fe_3O_4 PNCs is observed to slightly increase with increasing Fe_3O_4 nanoparticle loading within the glassy plateau (at 30 °C). This is due to the confinement of the Fe_3O_4 NPs in the matrix. The reason for the slight increase is due to the agglomeration of Fe_3O_4 NPs. Thus, the DMA data agree well with the rheological properties. A similar trend for E'' is observed as a function of temperature, Figure 2-6(B). The PS PNCs reinforced with 20 wt% Fe_3O_4 NPs within the glassy plateau range exhibit the highest E'' , which is increased from 83 to 90 °C as compared with that of the neat PS. This is attributed to the constrained friction between polymer chains after adding Fe_3O_4 NPs in the PS matrix.^[47]

Figure 2-6(C) depicts the temperature dependent $\tan\delta$ of neat PS and its PNCs. The $\tan\delta$ is the ratio of E'' to E' and the peak of $\tan\delta$ is often used to determine the glass transition temperature (T_g) of the materials. The T_g of the PNCs increases 2-3 °C compared with neat PS, and this is in agreement with the DSC results discussed in the previous section. This phenomenon is due to the segmental immobilization of matrix chains in the presence of Fe_3O_4 PNCs.^[48]

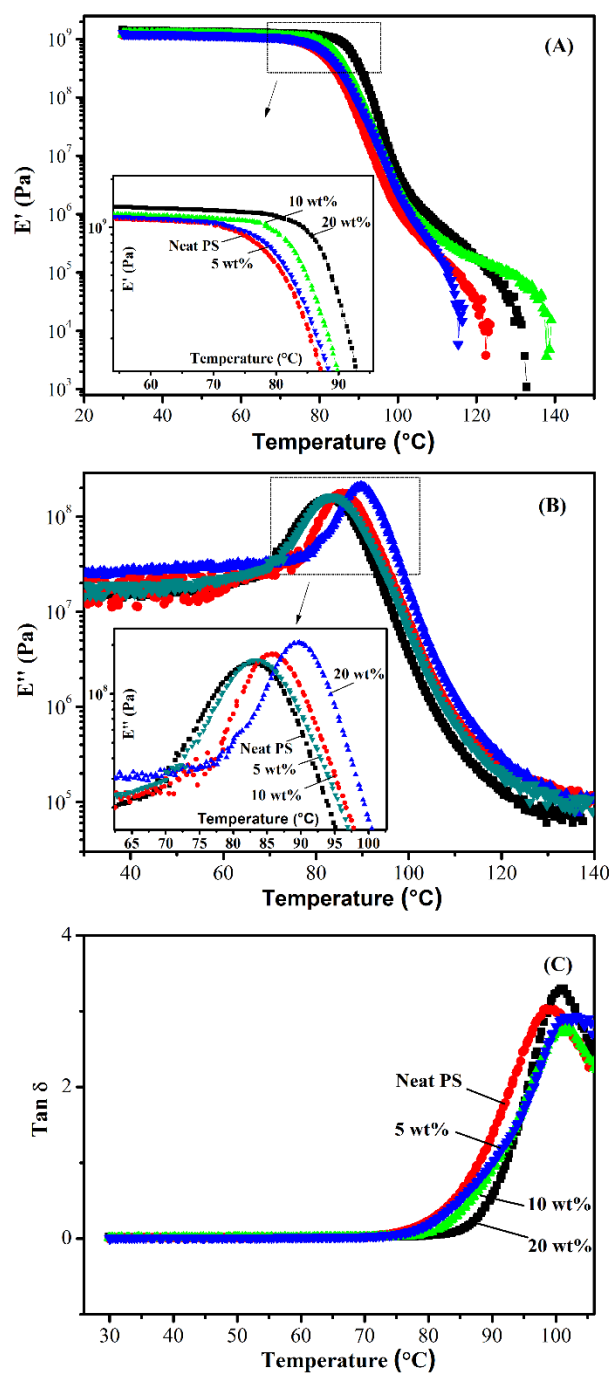


Figure 2-6. (A) Storage Modulus (E'), (B) loss modulus (E'') and (C) $\tan \delta$ vs. temperature for the neat PS and its nanocomposites with different Fe_3O_4 nanoparticle loadings.

2.3.7 Melt Rheological Behavior

The rheological behavior of the polymer nanocomposite melts are essential to further investigate the dynamics of the nanoconfined polymer. Also the formation of a percolated system can be detected by characterizing the storage modulus (G'), loss modulus (G''), mechanical loss factor ($\tan\delta$) and complex viscosity (η^*) as functions of frequency.^[49-51] The PS chains were fully relaxed in the absence of any NPs and revealed a typical homogeneous polymer-like terminal behavior on the basis of melting at 230 °C. G' is observed to increase monotonically with increasing particle loading over the whole frequency range (Figure 2-7(A)). The G' of PNCs with different particle loadings exhibits a larger enhancement at lower frequency than that at higher frequency, due to the presence of the NPs that restrain the large scale polymer chain relaxations in the PNCs if the frequency is low enough.^[44] Moreover, a percolation plateau was observed in the low frequency range (0.1-1 Hz) when the NPs were introduced into the matrix except the pure PS sample. However, G' of the PNCs with 20 wt% particle loading is lower than that of the PNCs with 10 wt% particle loading at low frequency, which indicates the dimensions of Fe₃O₄ NPs become large, leading to the decreased obstruction for polymer chain relaxations. Obviously, the effect of the particle loading on the rheological properties is relatively weak at high frequency, which indicates that the short range dynamics of the PS chains are not significantly affected by the NPs.^[20] A similar curve of G'' is observed to linearly increase upon incorporation of the NPs in the PS matrix and further increase with increasing the frequency in Figure 2-7(B).

Figure 2-7(C) shows $\tan\delta$ as a function of frequency. $\tan\delta$ is the ratio of G'' to G' , which is highly related to the applied frequency. When scanning the experimental frequency from low to high, $\tan\delta$ of the PNCs decreases with increasing particle loading. The higher $\tan\delta$ of neat PS compared to the PNCs is due to the free relaxation of the PS chains. After adding the NPs, the

polymer chain relaxation and relative motion have been greatly restrained. Furthermore, the higher the particle loading, the lower is $\tan\delta$. The reason is that the interaction between the NPs and the polymer matrix increases as the particle loading increases, which is in good agreement with the FT-IR results. In addition, a broad peak is observed in all the PNCs except the pure PS sample. The peak position shifts to higher frequency in the PNCs with 5 and 10 wt% particle loadings, which is due to the increased restrictions. However, the peak position of 20 wt% particle loading shifting to a lower frequency is due to the agglomeration of Fe_3O_4 NPs, which hinders the energy dissipation and relaxation between the NPS and polymer matrix.

Figure 2-7(D) illustrates the complex viscosity (η^*) of neat PS and its PNCs in a log-log plot of the viscosity as a function of frequency. The η^* is observed to increase with increasing particle loading, especially at low frequencies such as 0.1 Hz. The interaction between Fe_3O_4 and the PP matrix restricts the PS chain movements as the Fe_3O_4 particle loading increases. The decreased viscosity with increasing shear rate or frequency is defined as shear thinning.^[52] The PNCs with a particle loading of 5 wt% are much more viscous than that of neat PS at low frequency and exhibit strong shear thinning behavior; meanwhile, this property is more evident with increasing particle loadings. The similar value of η^* at high frequency (10-100 Hz) indicates polymer melt rather than NPs dominated fluid dynamics.

2.3.8 Magnetic Properties

Figure 2-8 shows the room temperature magnetic hysteresis loops of PS nanocomposites with different particle loadings. The insert of Figure 2-8 shows the as-received pure Fe_3O_4 NPs. The saturation magnetization (M_s) is defined as the state at which the magnetic field cannot

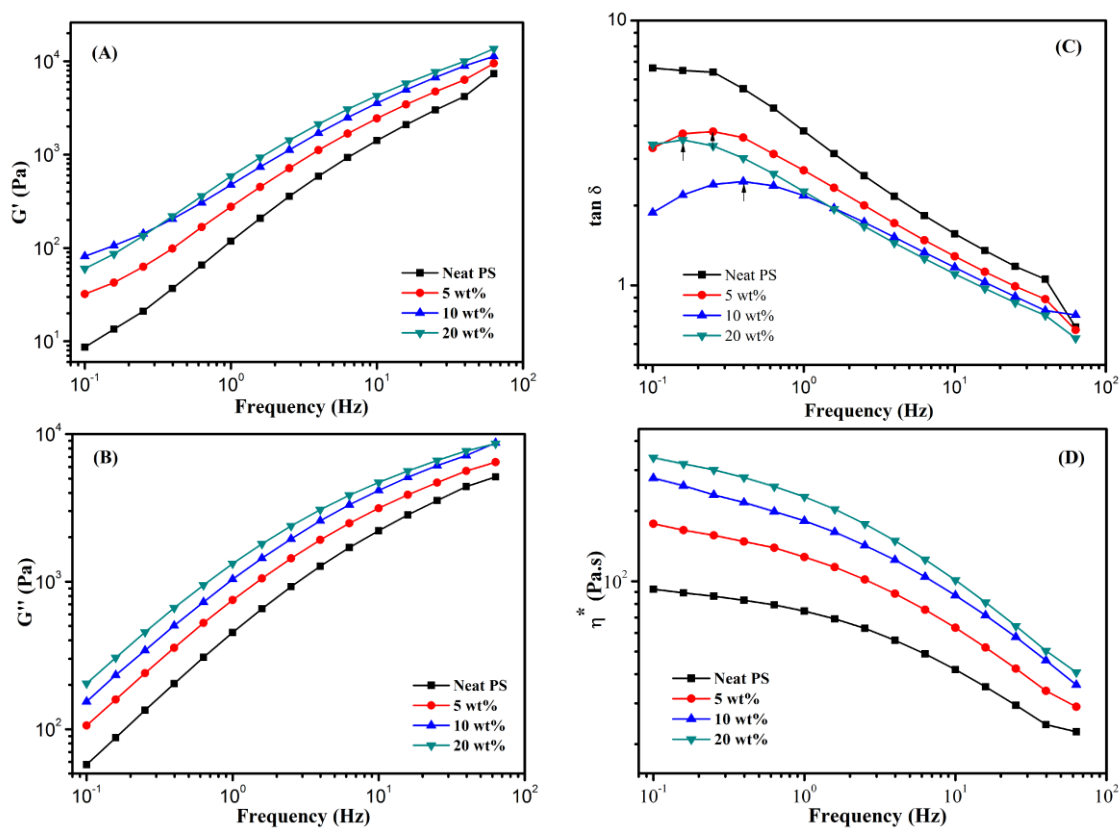


Figure 2-7. (A) Storage modulus (G'), (B) loss modulus (G''), (C) mechanical loss factor ($\tan \delta$) and (D) complex viscosity (η^*) as a function of frequency for PS and its PNCs.

increase the magnetization of the material further.^[20] The pure PS is observed to be non-magnetic as expected, whereas the curves of the others show no hysteresis loops. The M_s of the as-received Fe_3O_4 NPs was not obtained even at high magnetic field and was determined by the extrapolated saturation magnetization obtained from the intercept of $M \sim H^{-1}$ at high field.^[53,54] The PNCs do not show hysteresis loops with zero coercivity, which indicates superparamagnetic behavior at room temperature.^[55] The calculated M_s of the as-received Fe_3O_4 NPs is 57.38 emu g^{-1} , which is smaller than the bulk Fe_3O_4 ($92\text{-}100 \text{ emu g}^{-1}$).^[56] The M_s values of the PS/ Fe_3O_4 PNCs with particle loadings of 10 and 20 wt% are observed to be saturated at a lower field and are about 6.1 and 11.9 emu g^{-1} , respectively. In addition, the magnetization saturated more rapidly in the PNCs with a lower nanoparticle loading. The particle loadings for 10 and 20 wt% estimated from the M_s are calculated to be 10.6% and 20.7%, which is consistent with the results obtained from TGA. The field required to saturate the magnetization of the 20 wt% sample is exponentially large and beyond the limit of the measurement. An infinitesimal coercivity was observed in all the samples, which indicates a superparamagnetic behavior of the PS/ Fe_3O_4 PNCs.^[10]

2.3.8 Dielectric Properties

Various PS PNCs with Fe_3O_4 NPs have been investigated for their potential applications in energy storage through measuring their dielectric properties.^[57,58] Dielectric materials can be used to store electrical energy through charge separation, which occurs when the electron distributions are polarized by an applied external electric field.^[59] Figure 2-9(A) depicts the frequency dependent real permittivity (ϵ') of these PNCs at 25 °C. The ϵ' of neat PS is about 3.6. The ϵ' of the PS PNCs incorporated with 5, 10, and 20 wt% of Fe_3O_4 slightly increased to 4.2-5.0. In addition, for the PNCs with low permittivity, the value of ϵ' in the PS PNCs is virtually independent of the

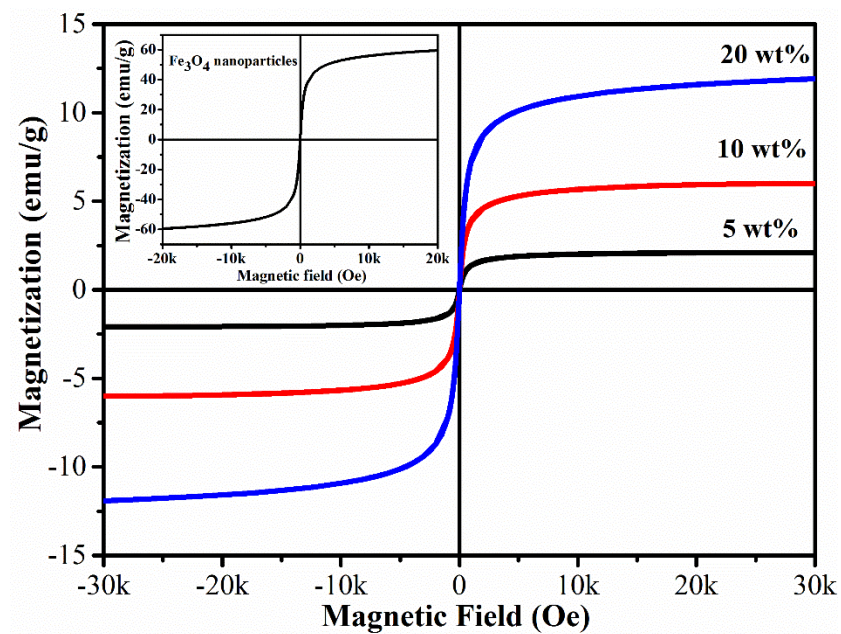


Figure 2-8. Room temperature hysteresis loops of PS/ Fe₃O₄ nanocomposites with a particle loading of 5, 10 and 20 wt%, respectively; insert shows pure NPs.

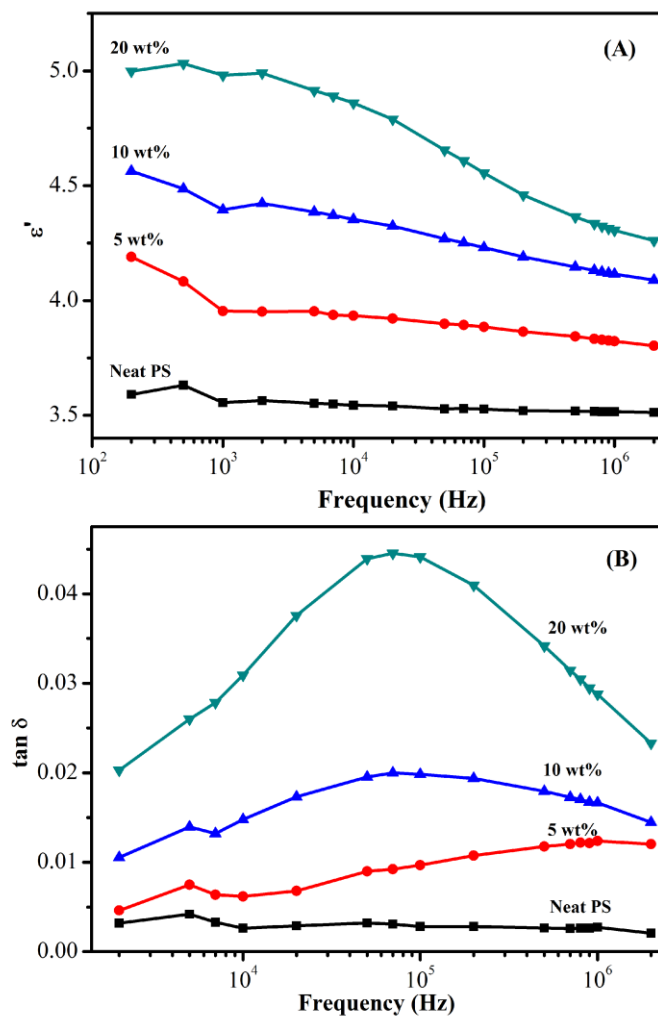


Figure 2-9. (A) Real permittivity, (B) dielectric loss tangent as a function of frequency for neat PS and its PNCS with different nanoparticle loadings.

frequency, indicating a stable dielectric performance of the prepared PNCs upon frequency variation. Their permittivity gradually decreased with increasing frequency and was stabilized at ca. 3.8, 4.2 and 4.4 for the PNCs with 5, 10 and 20 wt%, respectively, at frequencies higher than 10^6 Hz. The step-like decrease of the ϵ' toward high frequency is induced by the dielectric relaxation, suggesting that the established percolation network structure is not stable and easily affected by the external frequency disturbances, similar to the poly (vinylidene fluoride)/MWCNTs and elastomer/CNF PNCs.^[60,61]

Figure 2-9(B) shows the frequency dependent dielectric loss ($\tan\delta$). The $\tan\delta$ value was observed to be slightly enhanced in the PNC with a particle loading of 5 wt% and the $\tan\delta$ value fluctuated with increasing oscillation frequency. However, the curves of the nanocomposites filled with 10 and 20 wt% Fe_3O_4 nanoparticles reach a peak value at around 10^5 Hz from the low frequency. After that, both curves decrease toward high frequency. The peak in 20 wt% Fe_3O_4 PNC sample is sharper than that of 15 wt% Fe_3O_4 PNCs. These phenomena reveal that the insulating layer is unstable and can be easily affected by increased frequency. The insulating PS layer, which was wrapped physically on the surface of NPs, became thinner and not sufficient to hold the charge carriers of the Fe_3O_4 NPs.^[62] Since large amount of electric energy storage is required in mobile electronic devices, hybrid electric vehicles, stationary power systems and pulse power applications,^[58,63] there is growing attention in the study of the dielectric property of new materials.

2.4. Conclusion

In summary, PS/ Fe_3O_4 nanocomposites with different particle loadings have been prepared through a solvent extraction method and systematically studied. The NPs were well distributed in the PS matrix with 5, 10 and 20 wt% without obvious agglomeration in the micron dimension with

strong interaction between PS and NPs. In addition, the average crystallite size of the Fe_3O_4 NPs with a loading of 10 wt% is about 13.59 nm, and the intensity of these diffraction peaks of the Fe_3O_4 NPs becomes stronger with increasing the nanoparticle loadings. Meanwhile, the thermal stability of the PS/ Fe_3O_4 PNCs was enhanced and the flammability of the PS matrix was suppressed by adding these Fe_3O_4 NPs. Both the glass transition temperature (T_g) and the melting temperature (T_m) were increased with increasing Fe_3O_4 NPs loadings. The observed monotonically decreasing complex viscosity indicated a strong shear thinning behavior in the PNCs. Furthermore, the percolation took place in the low frequency range (0.1-1 Hz) when the NPs were introduced into the matrix. The PS/ Fe_3O_4 PNCs exhibit superparamagnetic behavior at room temperature. In addition enhanced dielectric properties were related to the Fe_3O_4 nanoparticle loadings.

2.5. References

- [1] P. Kim, N. M. Doss, J. P. Tillotson, P. J. Hotchkiss, M. J. Pan, S. R. Marder, J. Li, J. P. Calame, J. W. Perry, *ACS nano* **2009**, 3, 2581.
- [2] T. Shimada, K. Ookubo, N. Komuro, T. Shimizu, N. Uehara, *Langmuir* **2007**, 23, 11225.
- [3] T. Kashiwagi, F. Du, J. F. Douglas, K. I. Winey, R. H. Harris, J. R. Shields, *Nat. Mater.* **2005**, 4, 928.
- [4] Z. Guo, S.-E. Lee, H. Kim, S. Park, H. Hahn, A. Karki, D. Young, *Acta Mater.* **2009**, 57, 267.
- [5] Z. Guo, S. Park, H. T. Hahn, S. Wei, M. Moldovan, A. B. Karki, D. P. Young, *J. Appl. Phys.* **2007**, 101, 09M511.
- [6] Q. Dai, D. Berman, K. Virwani, J. Frommer, P. O. Jubert, M. Lam, T. Topuria, W. Imaino, A. Nelson, *Nano Lett.* **2010**, 10, 3216.
- [7] J. Zhu, S. Wei, L. Zhang, Y. Mao, J. Ryu, A. B. Karki, D. P. Young, Z. Guo, *J. Mater. Chem.* **2010**, 21, 342.
- [8] O. Breuer, U. Sundararaj, *Polym. Compos.* **2004**, 25, 630.
- [9] J. Zhu, S. Wei, D. Rutman, N. Haldolaarachchige, D. P. Young, Z. Guo, *Polymer* **2011**, 52, 2947.
- [10] X. Chen, S. Wei, C. Gunesoglu, J. Zhu, C. S. Southworth, L. Sun, A. B. Karki, D. P. Young, Z. Guo, *Macromol. Chem. Phys.* **2010**, 211, 1775.
- [11] B. Lin, G. A. Gelves, J. A. Haber, P. Pötschke, U. Sundararaj, *Macromol. Chem. Phys.* **2008**, 293, 631.
- [12] U. Lange, S. Ivanov, V. Lyutov, V. Tsakova, V. M. Mirsky, *J. Solid State Electrochem.* **2010**, 14, 1261.
- [13] J. Zhu, S. Wei, J. Ryu, L. Sun, Z. Luo, Z. Guo, *ACS Appl. Mater. Interfaces* **2010**, 2, 2100.
- [14] S. Khanna, S. Linderorth, *Phys. Rev. Lett.* **1991**, 67, 742.
- [15] X. Lin, C. Sorensen, K. Klabunde, G. Hadjipanayis, *Langmuir* **1998**, 14, 7140.
- [16] S. Apsel, J. Emmert, J. Deng, L. Bloomfield, *Phys. Rev. Lett.* **1996**, 76, 1441.
- [17] J. Zhu, S. Wei, J. Ryu, M. Budhathoki, G. Liang, Z. Guo, *J. Mater. Chem.* **2010**, 20, 4937.
- [18] Z. Guo, T. Y. Kim, K. Lei, T. Pereira, J. G. Sugar, H. T. Hahn, *Compos. Sci. Technol.* **2008**, 68, 164.
- [19] R. F. Ziolo, E. P. Giannelis, B. A. Weinstein, M. P. O'horo, B. N. Ganguly, V. Mehrotra, M. W. Russell, D. R. Huffman, *Science* **1992**, 257, 219.
- [20] J. Zhu, S. Wei, Y. Li, L. Sun, N. Haldolaarachchige, D. P. Young, C. Southworth, A. Khasanov, Z. Luo, Z. Guo, *Macromolecules* **2011**, 44, 4382.
- [21] B. Zapotoczny, M. Dudek, J. Koziol, J. Mleczko, *Phys. A* **2013**, 392, 1493.
- [22] Z. Huang, F. Tang, *J. Colloid Interface Sci.* **2004**, 275, 142.
- [23] J.-l. Zhao, R. Yi, *Polym. Mater. Sci. Eng.* **2009**, 10, 30.
- [24] W. Zhong, P. Liu, H. Shi, D. Xue, *Express Polym. Lett* **2010**, 4, 183.
- [25] D. Shi, H. S. Cho, Y. Chen, H. Xu, H. Gu, J. Lian, W. Wang, G. Liu, C. Huth, L. Wang, *Adv. Mater.* **2009**, 21, 2170.
- [26] J. Sun, S. Zhou, P. Hou, Y. Yang, J. Weng, X. Li, M. Li, *J. Biomed. Res. A* **2007**, 80, 333.
- [27] J. Zhang, J. Chen, Z. Wang, *Mater. Lett.* **2007**, 61, 1629.
- [28] J. Deng, X. Ding, W. Zhang, Y. Peng, J. Wang, X. Long, P. Li, A. S. C. Chan, *Polymer* **2002**, 43, 2179.
- [29] L. Qiu, W. Chen, B. Qu, *Polym. Degrad. Stab.* **2005**, 87, 433.

- [30] D. Wu, X. Ge, Y. Huang, Z. Zhang, Q. Ye, *Mater. Lett.* **2003**, 57, 3549.
- [31] D. Wu, X. Ge, Z. Zhang, M. Wang, S. Zhang, *Langmuir* **2004**, 20, 5192.
- [32] M. Mahmoudi, A. Simchi, M. Imani, A. S. Milani, P. Stroeve, *Nanotechnology* **2009**, 20, 225104.
- [33] L. M. Liz-Marzan, P. V. Kamat, *Nanoscale Materials*, Springer, **2003**.
- [34] M. Xiao, L. Sun, J. Liu, Y. Li, K. Gong, *Polymer* **2002**, 43, 2245.
- [35] B. N. Jang, M. Costache, C. A. Wilkie, *Polymer* **2005**, 46, 10678.
- [36] Q. Zhao, E. T. Samulski, *Polymer* **2006**, 47, 663.
- [37] K. Saeed, S. Y. Park, H. J. Lee, J. B. Baek, W. S. Huh, *Polymer* **2006**, 47, 8019.
- [38] A. Chatterjee, B. Deopura, *J. Appl. Polym. Sci.* **2006**, 100, 3574.
- [39] T. Monakhova, P. Nedorezova, T. Bogayevskaya, V. Tsvetkova, Y. A. Shlyapnikov, *Polym. Sci. USSR* **1988**, 30, 2589.
- [40] P. Uthirakumar, K. S. Nahm, Y. B. Hahn, Y. S. Lee, *Eur. Polym. J.* **2004**, 40, 2437.
- [41] K. Wakabayashi, P. J. Brunner, J. Masuda, S. A. Hewlett, J. M. Torkelson, *Polymer* **2010**, 51, 5525.
- [42] V. Babrauskas, R. D. Peacock, *Fire Saf. J.* **1992**, 18, 255.
- [43] C. Q. Yang, Q. He, R. E. Lyon, Y. Hu, *Polym. Degrad. Stab.* **2010**, 95, 108.
- [44] D. W. Chae, K. J. Kim, B. C. Kim, *Polymer* **2006**, 47, 3609.
- [45] H. Gu, S. Tadakamalla, Y. Huang, H. A. Colorado, Z. Luo, N. Haldolaarachchige, D. P. Young, S. Wei, Z. Guo, *ACS Appl. Mater. Interfaces* **2012**, 4, 5613.
- [46] H. B. Hsueh, C. Y. Chen, *Polymer* **2003**, 44, 5275.
- [47] T. Liu, I. Y. Phang, L. Shen, S. Y. Chow, W.-D. Zhang, *Macromolecules* **2004**, 37, 7214.
- [48] S. K. Nayak, S. Mohanty, *J. Appl. Polym. Sci.* **2009**, 112, 778.
- [49] J. Zhu, S. Wei, A. Yadav, Z. Guo, *Polymer* **2010**, 51, 2643.
- [50] P. Pötschke, M. Abdel-Goad, I. Alig, S. Dudkin, D. Lellinger, *Polymer* **2004**, 45, 8863.
- [51] C. A. Mitchell, J. L. Bahr, S. Arepalli, M. James, R. Krishnamoorti, *Macromolecules* **2002**, 35, 8825.
- [52] M. Sugimoto, T. Tanaka, Y. Masubuchi, J. I. Takimoto, K. Koyama, *J. Appl. Polym. Sci.* **1999**, 73, 1493.
- [53] Z. Guo, L. L. Henry, V. Palshin, E. J. Podlaha, *J. Mater. Chem.* **2005**, 16, 1772.
- [54] D. Zhang, A. B. Karki, D. Rutman, D. P. Young, A. Wang, D. Cocke, T. H. Ho, Z. Guo, *Polymer* **2009**, 50, 4189.
- [55] S. Xuan, L. Hao, W. Jiang, X. Gong, Y. Hu, Z. Chen, *J. Magn. Magn. Mater.* **2007**, 308, 210.
- [56] P. Hu, S. Zhang, H. Wang, D. Pan, J. Tian, Z. Tang, A. A. Volinsky, *J. Alloys Compd.* **2011**, 509, 2316.
- [57] X. Chen, S. Wei, A. Yadav, R. Patil, J. Zhu, R. Ximenes, L. Sun, Z. Guo, *Macromol. Mater. Eng.* **2011**, 296, 434.
- [58] H. S. Nalwa, *Handbook of Low and High Dielectric Constant Materials and Their Applications, Two-Volume Set*, Academic Press, **1999**.
- [59] P. Barber, S. Balasubramanian, Y. Anguchamy, S. Gong, A. Wibowo, H. Gao, H. J. Ploehn, H. C. Zur Loye, *Materials* **2009**, 2, 1697.
- [60] J. Zhu, S. Wei, J. Ryu, Z. Guo, *J. Phys. Chem. C* **2011**, 115, 13215.
- [61] Z. M. Dang, L. Wang, Y. Yin, Q. Zhang, *Adv. Mater.* **2007**, 19, 852.
- [62] Q. He, T. Yuan, J. Zhu, Z. Luo, N. Haldolaarachchige, L. Sun, A. Khasanov, Y. Li, D. P. Young, S. Wei, *Polymer* **2012**, 53, 3642.

- [63] T. Ōsaka, M. Datta, *Energy Storage Systems in Electronics, Vol. 1*, CRC PressI Llc, **2000**.

Chapter 3. Surface Coating of Sub-microspherical Polymer with Gold Nanoparticles

Abstract

A novel type of crystalline gold (Au) nanoparticle (NP) coated composite sub-micrometer spheres of poly(glycidyl methacrylate) (PGMA) with a layer of poly(allylamine hydrochloride) (PAH) film was prepared by an easily controlled assembly method. The Au NPs exhibited a discontinuous structure on the PGMA@PAH particle surface exhibiting a surface interaction between PGMA spheres and Au NPs. PAH not only modified the surface of the PGMA particles but also positively affected the crystallite of the PGMA particles. The real permittivity of the nanocomposite spheres was much higher than that of pure PGMA spheres. An improved thermal stability was observed in the nanocomposite spheres. The calculated band gap (0.91 eV) of the nanocomposite spheres was observed to be lower than that (4.92 eV) of pure PGMA spheres.

3.1. Introduction

Micron-sized monodispersed polymer particles have attracted increasing interest from both academic scholars and industrial researchers owing to their complex properties and extensive applications in coatings, paints, packaging, photonic crystals, chemical and biological sensors, drug delivery, bio-separation, chromatography and microelectronics.^[1-9] Several techniques have been explored for preparing monodispersed polymer particles with miscellaneous sizes, such as the activation method,^[5] successive seeding method,^[10,11] dispersion polymerization,^[12-15] heterogeneous polymerization,^[16] sol-gel method,^[17] and surfactant-free emulsion polymerization.^[18-22] Among them, the surfactant-free emulsion polymerization method has been successfully applied for synthesizing functionalized polymer colloids with controlled sizes from several hundred nanometers to several micrometers. Physicochemical properties of these polymer microspheres can be significantly improved by the core-shell structures,^[23] which can be obtained by coating with multiple functional materials including graphene oxide (GO),^[24] carbon nanotubes (CNTs),^[25] zinc oxide (ZnO),^[26] nickel,^[27] polypyrrole (PPy)^[28] and gold^[29] for plentiful novel technological applications. Due to their distinguished and effective catalytic,^[30] electronic,^[31] biolabeling^[32, 33] and optical properties,^[34] gold (Au) nanoparticles (NPs) have received more attention in the past few years. However, the reported composite substrates are mainly based on chemically inert materials including polystyrene, polypropylene or poly(methyl methacrylate), which limit the development of new novel functional materials. The homopolymer and copolymers of glycidyl methacrylate (GMA) belong to the class of functional polymers. One of the representatives is poly(glycidyl methacrylate) (PGMA). The facile reaction of the epoxy groups with a large variety of reagents provides a novel route to prepare various multifunctional polymers through chemical modifications of these polymers. For example, Kim et al.^[35] fabricated a cross-

linked PGMA coating on soft magnetic carbonyl iron particles (CIPs) by dispersion polymerization to study the magnetorheological (MR) properties. Xu et al.^[36] reported that the PGMA particles coated capillary column can provide more retention and higher resolution for analytes after functionalization. However, Au nanoparticle-reinforced PGMA polymer nanocomposites (PNCs) have rarely been reported, especially on the optical and dielectric properties.

In this study, sub-micrometer scale PGMA composite spheres coated with fairly uniformly dispersed gold nanoparticles were successfully prepared by a simple and readily controlled assembly method. The effect of the gold nanoparticles on the crystallization behaviors of PGMA spheres was studied by X-ray diffraction (XRD). The morphologies of the PGMA@PAH@AuNPs spheres and gold nanoparticles were investigated by TEM. The chemical structures of the PGMA, PGMA@PAH and PGMA@PAH@AuNPs spheres were also characterized by Fourier transform infrared (FT-IR) spectroscopy. The optical properties of PGMA@PAH@AuNPs were investigated by UV-vis spectroscopy and the corresponding bandgap was calculated. The thermal stability and dielectric properties were also studied and discussed.

3.2. Experimental

3.2.1 Materials

0.005% Mequinol stabilizer was removed from glycidyl methacrylate ($\geq 97.0\%$, Sigma-Aldrich, St. Louis, MO, USA) with an inhibitor remover (Sigma-Aldrich, St. Louis, MO, USA) prior to usage. Potassium persulfate (KPS) ($99+\%$), poly(allylamine hydrochloride) (PAH) ($M_w = 15,000$) trisodium citrate and hydrogen tetrachloroaurate trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) ($\geq 99.9\%$) were purchased from Sigma-Aldrich and used as received without any further treatment. Nanopure

water (18 M Ω cm) was supplied by Barnstead. The cellulose ester dialysis membrane (MWCO 3500-5000, 80000-100000) was provided by Spectrum Laboratory, Inc, Rancho Dominguez, CA.

3.2.2 Preparation of Composites

a) Synthesis of Poly(glycidyl methacrylate) Colloidal Spheres

Monodispersed colloidal poly(glycidyl methacrylate) particles with a diameter of 448 ± 9 nm were synthesized by a modified surfactant-free emulsion polymerization method, as described in the prior literature.^[18] In brief, 15 mL inhibitor-free glycidyl methacrylate (GMA) was dispersed in 150 mL nanopure water purged with N₂ by stirring vigorously at 1,200 rpm for 30 min at room temperature. Then the mixture was refluxed and heated to 90 °C following dropwise addition of 0.5 g KPS dissolved in 10 mL water. The nitrogen flow was adjusted to minimize the stripping of monomers from the reaction mixture. The stirring rate of 1,200 rpm and temperature of 90 °C were maintained constant until the end of the reaction. After a 2-hour reaction period, the reaction was completed by bubbling oxygen for 30 min and the product was cooled down to room temperature. 10 mL PGMA spheres were dialyzed with a cellulose ester dialysis membrane for 24 hours and centrifuged at 5,000 rpm for 30 min. After three successive centrifugation/wash cycles with nanopure water, the purified PGMA spheres were acquired.

b) Preparation of PGMA@PAH Particles

The PGMA spheres were adsorbed with a weak hydrophobic polyelectrolyte using positively charged PAH solution by the deposition technique, which was introduced by Liu et al.^[37] 1 mL 0.75% (w/v) PAH solution was added to 10 mL purified PGMA spheres suspended solution to provide a positively charged layer to facilitate the subsequent adsorption of negatively charged

gold nanoparticles. The mixture was further dialyzed with a cellulose ester dialysis membrane (MWCO 80,000-100,000) for 24 hours to remove the redundant PAH. Then the PAH-modified PGMA cores were separated from the supernatant by centrifugation for 30 min at 5,000 rpm; 11 mL nanopure water was used to clean the product. After three successive centrifugation/wash cycles with nanopure water, the PGMA@PAH particles were obtained.

c) Formation of PGMA@PAH@AuNPs Composites

According to the Turkevich method,^[38] hydrogen tetrachloroaurate trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) as the gold precursor and trisodium citrate as reductant were used to synthesize gold (Au) nanoparticles (NPs). Briefly, 250 mL 1 mM $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ was heated to its boiling point, and 25 mL 38.3 mM trisodium citrate was then added. When changed from colorless to ruby-red, the solution was removed from heat, and allowed to cool down to room temperature. The centrifuged PGMA@PAH spheres were dispersed in 11 mL nanopure water with pH = 7. To form the Au nanoparticles coated PGMA composite spheres, 60 μL PGMA@PAH was added to 3 mL as-synthesized gold nanoparticle solution. The product was mixed by gently shaking at around 1,000 rpm for 30 min. After centrifugation and re-dispersion in nanopure water, the PGMA@PAH@Au nanocomposites were collected.

3.2.3 Characterization

The crystalline structure of PGMA, PGMA@PAH and PGMA@PAH@AuNPs was studied by X-ray diffraction (XRD), which was carried out by a Bruker AXS D4 Endeavor diffractometer operating with a Cu $K\alpha$ radiation source filtered with a graphite monochromator (0.154 nm). The samples were pressed in a sample holder. The X-ray was generated at 40 kV and 40 mA power and XRD scans were recorded at 2θ from 5 to 80 ° with a 1 °/min scan rate.

The morphologies of the PGMA@PAH@AuNPs were characterized by transmission electron microscope (TEM) (JEM-1400) at an accelerating voltage of 120 kV and high-resolution TEM (HRTEM) images were visualized on a transmission electron microscope (JEOL JEM2100F) at an accelerating voltage of 200 kV.

The Fourier transform infrared (FTIR) spectra of the products were obtained by using a Bruker Tensor 27 FT-IR spectrometer with Hyperion 1000 attenuated total reflection (ATR) microscopy accessory in the range of 500-4000 cm^{-1} at a resolution of 4 cm^{-1} .

The thermal stability of PGMA, PGMA@PAH and PGMA@PAH@AuNPs was investigated by thermogravimetric analysis (TGA, TA-Q500 instrument). Samples were heated from room temperature to 600 $^{\circ}\text{C}$ at a constant heating rate of 10 $^{\circ}\text{C} \cdot \text{min}^{-1}$ under air and nitrogen gas atmosphere, respectively. The flow rate was 60 $\text{mL} \cdot \text{min}^{-1}$ under both atmospheres.

Dielectric properties of pure PGMA and its nanocomposites were measured by an Agilent E4980A LCR Meter equipped with an Agilent E4980B dielectric test fixture in the frequency range from 20 to 2M Hz at room temperature. The samples used were prepared from a pressing machine (Carver, Model 3853-0) with 15,000 pounds for 15 min at room temperature and were 25 mm in the diameter and ~ 2.0 mm in the thickness.

The optical properties were characterized using ultraviolet-visible diffuse reflectance spectroscopy techniques (Jasco V-670 spectrophotometer equipped with a Jasco ISN-723 diffuse reflectance accessory). The samples for this test were prepared following the same procedures as used for the dielectric property test.

3.3. Results and Discussion

3.3.1 X-ray Diffraction

Figure 3-1 shows the XRD patterns of the PGMA, PGMA@PAH and PGMA@PAH@AuNPs composites. For the crystalline structures, the XRD patterns can be used to evaluate the average crystallite size, lattice plane d -spacing and crystallinity. The PGMA particles mainly exhibit a strong reflection at $2\theta = 17.5^\circ$. The average crystallite size can be estimated from XRD pattern^[39] by the Scherrer Equation (1):

$$L = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where L is the average crystallite size, k is the shape factor, λ is the X-ray wavelength ($\lambda = 0.154$ nm), β is the full width at half maximum (FWHM), and θ is the angle at maximum intensity. The value of k depends on several factors, including the Miller index of the reflection plane and the shape of the crystal, which is normally 0.89. Here, the average crystallite size of the PGMA particles is about 1.6647 nm at $2\theta = 17.5^\circ$. Meanwhile, the average crystallite size of the PGMA@PAH particles is around 1.6741 nm at $2\theta = 18.5^\circ$. With the comparison of the peak position and average crystallite size, PAH not only modified the surface of the PGMA particles (Figure 3-2), but also positively affected the crystallite of the PGMA particles. Furthermore, the average crystallite size of the PGMA@PAH@AuNPs particles is around 1.8618 nm at $2\theta = 18.5^\circ$, indicating that the addition of the Au nanoparticles changed the original crystal structure of the PGMA@PAH particles. Apparently, the three sharp diffraction peaks of the PGMA@PAH@AuNPs particles are observed at $2\theta = 38.2, 44.5$ and 64.7 , which correspond to

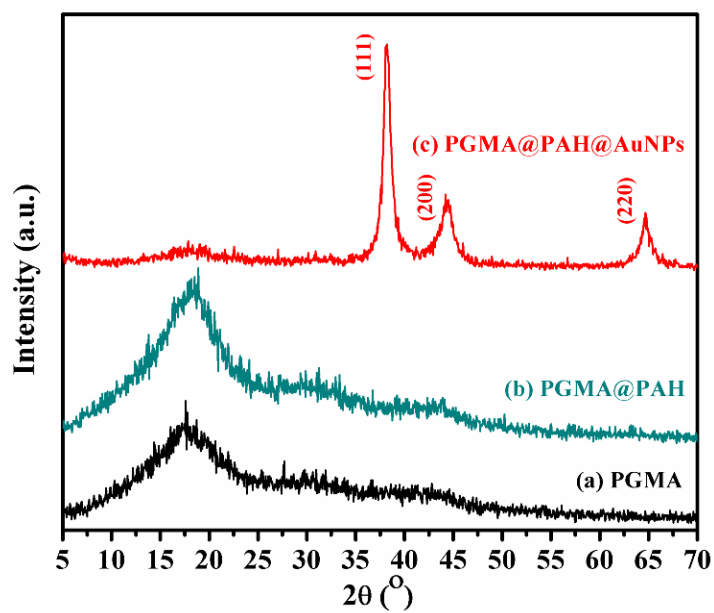


Figure 3-1. XRD patterns of the (a) PGMA, (b) PGMA@PAH and (c) PGMA@PAH@AuNPs sub-microspheres.

(111), (200) and (220) crystallographic plans of face-centered cubic (fcc), respectively,^[40-42] indicating that the gold nanoparticles have successfully coated on the PGMA@PAH particles.

3.3.2 TEM Micrographs

The morphology of the PGMA@PAH@AuNPs particles is essential to better understand the unique performance of this material. The dispersion and identification of the nanoparticles are characterized by TEM. A discontinuous inorganic shell coated on the organic colloidal beads was observed (Figure 3-2a). The PGMA spheres of 448 nm in diameter are coated with gold nanoparticles with a diameter of 12 ± 3 nm. In this composite structure, the immobilization of metal nanoparticles on the spherical substrates provides benefits not only in the easy deployment of nanoparticles during applications but also in maintaining their size effects. The crystallinity of the gold nanoparticles was also studied by high-resolution TEM (Figure 3-2b). The lattice plane spacings of 0.236, 0.204, 0.144 nm were indexed to the (111), (200), (220) planes of the face-centered-cubic (fcc) crystal gold, respectively. This result was in good agreement with XRD results. Considering the observed orientation of the lattice plane, the gold nanoparticles displayed a polyhedral morphology.^[43]

3.3.3 FT-IR Spectra

Figure 3-3 depicts the FT-IR spectra of the PAH, PGMA, PGMA@PAH and PGMA@PAH@AuNPs composites, respectively. Two characteristic peaks for the epoxy group ring were obtained from PGMA, PGMA@PAH and PGMA@PAH@AuNPs composites: 1,260 cm^{-1} corresponding to the stretching and contracting in-phase of the epoxy group ring bonds, 850 cm^{-1} corresponding to the asymmetric vibrations of the epoxy rings.^[18,44,45] However, the PGMA@PAH@AuNPs composites have a peak shift from 850 to 836 cm^{-1} , indicating the surface interaction between PGMA spheres and gold nanoparticles. Moreover, the absorption peaks at

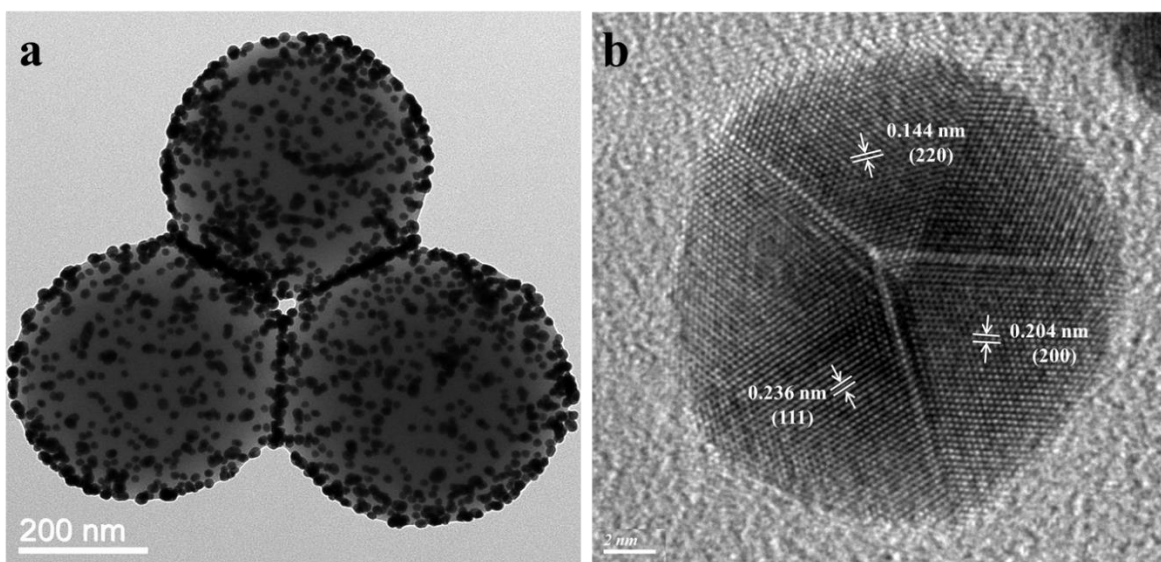


Figure 3-2. (a) TEM of PGMA@PAH@AuNPs particles, and (b) high-resolution TEM of gold nanoparticles.

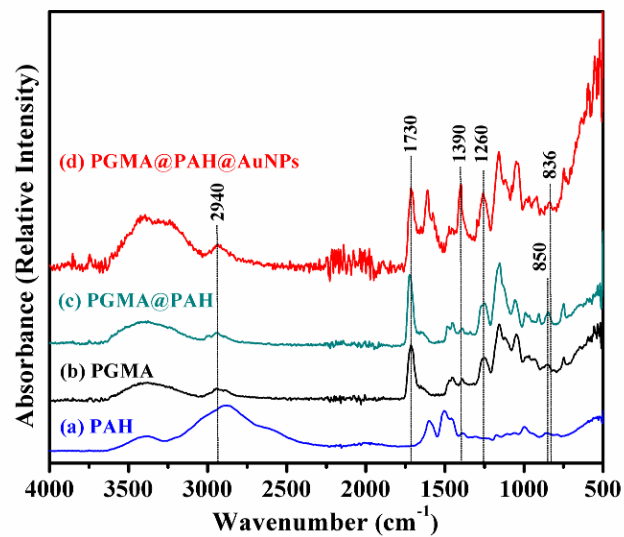


Figure 3-3. FT-IR spectra of the (a) PAH, (b) PGMA, (c) PGMA@PAH and (d) PGMA@PAH@AuNPs composites, respectively.

1,730 and 1,390 cm^{-1} were attributed to the C=O and C–O stretching vibration of the ester group of the PGMA sub-microspheres.^[24] In addition, the C–H stretching in the methyl and methylene group in the PGMA composites was observed at 2,940 cm^{-1} .^[46] Furthermore, a broad absorption band associated with O–H stretching vibrations of the hydroxyl group was also found at around 3,390 cm^{-1} .^[47,48] These results demonstrated that the PGMA composites have been successfully synthesized.

3.3.4 Thermogravimetric Analysis

Figure 3-4 (a, b, c, d) shows the TGA weight loss and corresponding derivative weight loss curves of PGMA, PGMA@PAH and PGMA@PAH@AuNPs sub-microspheres under both air and nitrogen flow conditions, respectively, the detailed thermal decomposition temperatures are shown in Table 3-1. Here, the T_{-10} is defined as the temperature at 10% weight loss of the tested specimen; and the $T_{-50\%}$ is defined as the temperature at half weight loss of the tested specimen. Normally, the first weight loss stage from room temperature to 100 °C is attributed to the release of moisture in the samples, which was confirmed by FT-IR results.^[49]

Under air atmosphere, the TGA measurements were used to investigate the influences of the gold nanoparticles on the thermal oxidative degradation of the PGMA matrix. The PGMA shows the temperature at a 10% weight loss ($T_{-10\%}$) of 222.0 °C, while the PGMA@PAH and PGMA@PAH@AuNPs composites show higher $T_{-10\%}$ at 244.0 and 271.0 °C, respectively (Figure 3-4(a)). The increased thermal stability of the PGMA@PAH@AuNPs composites indicates the increased interaction between PGMA polymer chains after the modification of PAH and the enhancing interface bonding strength between the PGMA polymer surface chains and the gold

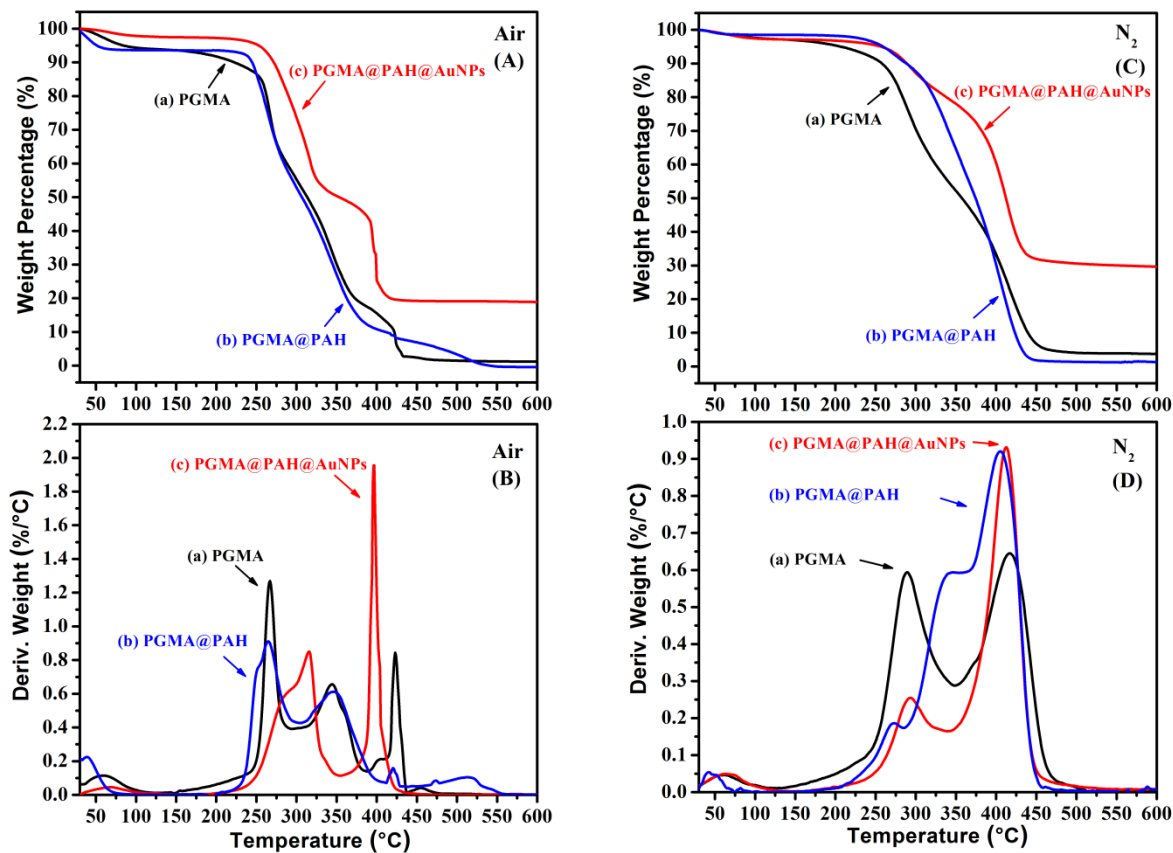


Figure 3-4. TGA weight loss curves of (a) PGMA, (b) PGMA@PAH and (c) GMA@PAH@AuNPs composites under (A) air and (C) nitrogen, and the corresponding derivative weight loss curves (B) and (D)

Table 3-1. TGA characteristics of the measured samples under both air and nitrogen flow conditions.

Atmosphere	Compositions	$T_{-10\%}$ [°C]	$T_{-50\%}$ [°C]	Residue at 600 °C (%)
Air	PGMA	222.0	313.0	1.2
	PGMA@PAH	244.0	306.0	0.0
	PGMA@PAH@AuNPs	271.0	353.0	18.9
N ₂	PGMA	258.0	357.0	3.7
	PGMA@PAH	282.0	374.0	1.3
	PGMA@PAH@AuNPs	288.0	412.0	29.6

nanoparticles at around 200–300 °C. From Figure 3-4(b), three peaks of PGMA, PGMA@PAH and PGMA@PAH@AuNPs composites were obtained; however, peaks of the PGMA@PAH@AuNPs composites have shifted obviously compared with those of the PGMA and PGMA@PAH composites. At low temperatures, gold particles inhibit the oxidation effect leading to an improved thermal stability of PGMA@PAH@AuNPs at around 280 °C compared with that of PGMA and PGMA@PAH at 260 °C; at higher temperatures, the gold nanoparticles act as a good heat conductor to transfer more energy to decompose the polymer chains more easily with an increase of temperature to enlarge the oxidation effect on the PGMA molecular chains. Hence the second and third peaks of the PGMA@PAH@AuNPs composites show a lower temperature than those of both PGMA and PGMA@PAH composites.

Under N₂ atmosphere, the PGMA spheres began to decompose with a 10% weight loss at 285 °C, and achieved a full decomposition at approximately 413 °C with little residue left (3.7%). For the PGMA@PAH@AuNPs sub-microspheres, the $T_{-10\%}$ and $T_{-50\%}$ were both increased to 228.0 and 412.0 °C, respectively (Figure 3-4(c) and Table 3-1). From Figure 3-4(d), the PGMA and PGMA@PAH@AuNPs have two peaks at around 300 and 425 °C respectively, which are consistent with the results reported for poly(methyl methacrylate) (PMMA).^[50,51] It can be concluded that the presence of oxygen significantly decreases the thermal stability of pure PGMA, and the thermal stability of the PGMA is enhanced with the introduction of gold nanoparticles.

3.3.5 Dielectric Properties

The PGMA and PGMA@PAH@AuNPs sub-microspheres have been investigated for their potential applications in energy storage through measuring their dielectric properties.^[52] Dielectric materials can be used to store electrical energy through charge accumulation/separation, which

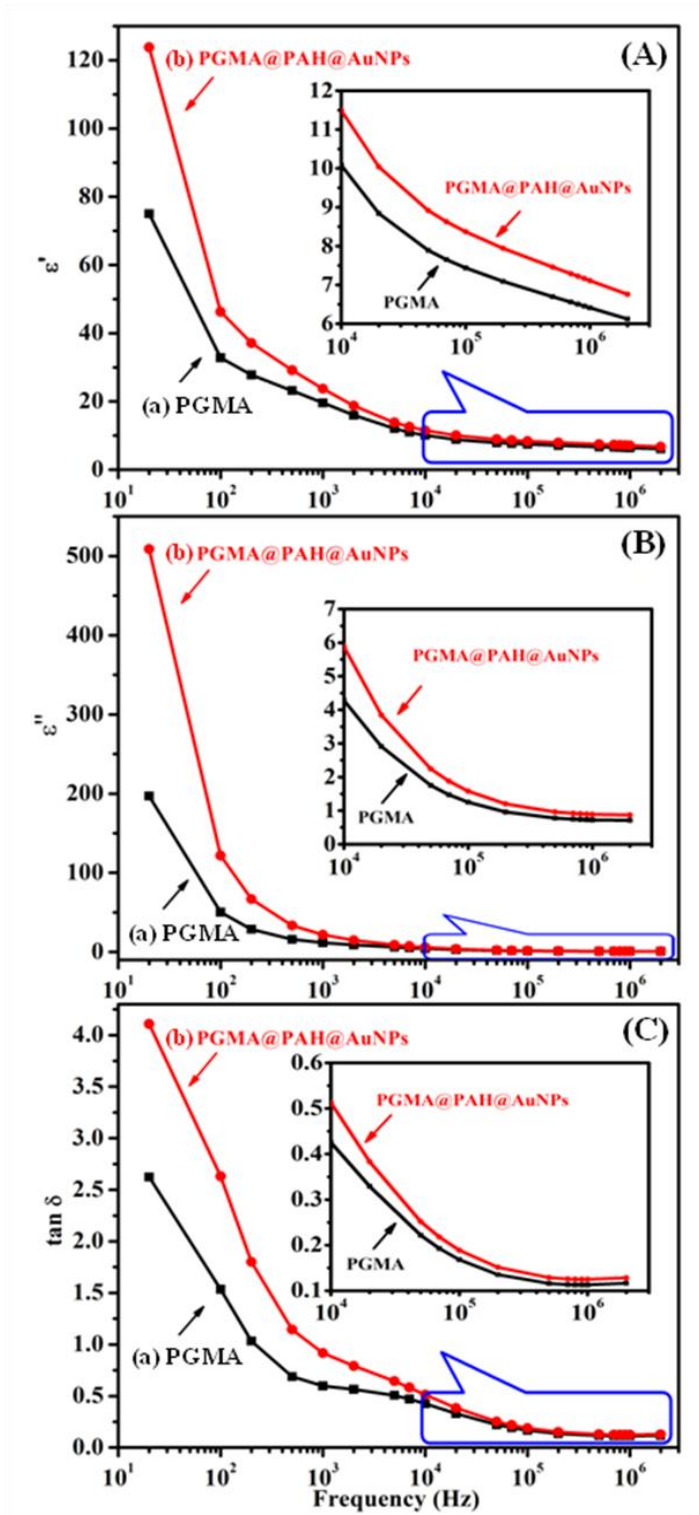


Figure 3-5. (A) Real permittivity (ϵ'), (A) imaginary permittivity (ϵ'') and (C) dielectric loss tangent ($\tan \delta$) as a function of frequency for (a) PGMA and (b) PGMA@PAH@AuNPs sub-microspheres.

occurs when the electron distributions are polarized by an applied external electric field.^[53] Figure 3-5(a) depicts the frequency dependent real permittivity (ϵ') of the PGMA and PGMA@PAH@AuNPs sub-microspheres at room temperature. As shown, the ϵ' value of the PGMA and PGMA@PAH@AuNPs sub-microspheres decreases with increasing the frequency, revealing a dielectric relaxation behavior.^[54] In addition, the PGMA@PAH@AuNPs sub-microspheres were observed to have a relatively higher ϵ' value than that of the PGMA sub-microspheres, and this phenomenon was more obvious at low frequency than that at high frequency, which is attributed to high conductivity of the Au nanoparticles. Due to the polarization of the interfaces between PGMA and AuNPs, the number of the accumulated charges will increase. Therefore, the real permittivity of the composites is higher than that of pure PGMA spheres. Other literature has reported the same results in different materials, such as Poly(vinylidene fluoride) (PVDF)-multiwalled carbon nanotube (MWNT) composites prepared by a coagulation method^[55] and novel ferroelectric PVDF composites prepared by a very simple blending and hot-molding technique.^[56]

Figure 3-5(c) shows the frequency dependent dielectric loss ($\tan\delta$) of the composites. It is worth noting that there is a higher dielectric loss in the PGMA@PAH@AuNPs sub-microspheres, which can be ascribed to a large electrical conduction loss in the Au-containing composites. The gold nanoparticles coated on the PGMA spheres as a discontinuous structure have a significant effect on the measured dielectric properties. Since a large amount of electric energy storage is required in mobile electronic devices, hybrid electric vehicles, stationary power systems and pulse power applications, there is a growing attention in the study of the dielectric properties of new materials. ^[57,58]

3.3.6 Optical Properties

The optical properties are some of the most important properties of materials in applications such as thin film transistors,^[59] solar cells,^[60] and chemical/biochemical sensors.^[61] The UV-vis diffuse reflection spectrum of the PGMA and PGMA@PAH@AuNPs sub-microspheres is shown in Figure 3-6. Compared with the spectrum of the PGMA spheres, the PGMA@PAH@AuNPs sub-microspheres exhibit a broad absorption peak at around 500 nm, which is close to the reported 528 nm for gold nanospheres.^[62] The peak at around 500 nm is due to not only the presence of gold nanoparticles, but also the size, shape and dielectric environment of the composites.^[63] Furthermore, the E_g values of the spheres were calculated from a photon-energy ($h\nu$) dependence of $\alpha h\nu$ converted from the diffuse reflectance UV-Vis spectra by Equation (2) (Tauc's plot^[64]):

$$\alpha h\nu = (h\nu - E_g)^n \quad (2)$$

where α , h , ν , and E_g is the absorbance coefficient, Planck constant, photon frequency, and photonic energy band gap, respectively. The parameter n depends on the nature of transition ($n=1/2$, 2, 3/2 or 3 for the allowed direct, allowed indirect, forbidden direct, or forbidden indirect transitions, respectively).^[65] The allowed direct band gap of the PGMA and PGMA@PAH@AuNPs sub-microspheres is also shown in Figure 3-6. The band gap of PGMA spheres is found to be 4.92 eV (Figure 3-6a), which is close to the reported 5 eV for the polymer materials.^[66] It is worth noting that the PGMA@PAH@AuNPs spheres exhibit a much lower band gap of 0.91 eV (Figure 3-6b), which can be applied for semiconductors.^[67] The reason for this discovery can be understood in terms of the quantum states for electrons. By the Pauli exclusion principle, each of states contains zero or one electron.^[68] Electrical conductivity takes place because of the presence of electrons in the states that are delocalized. However, an electron orbital

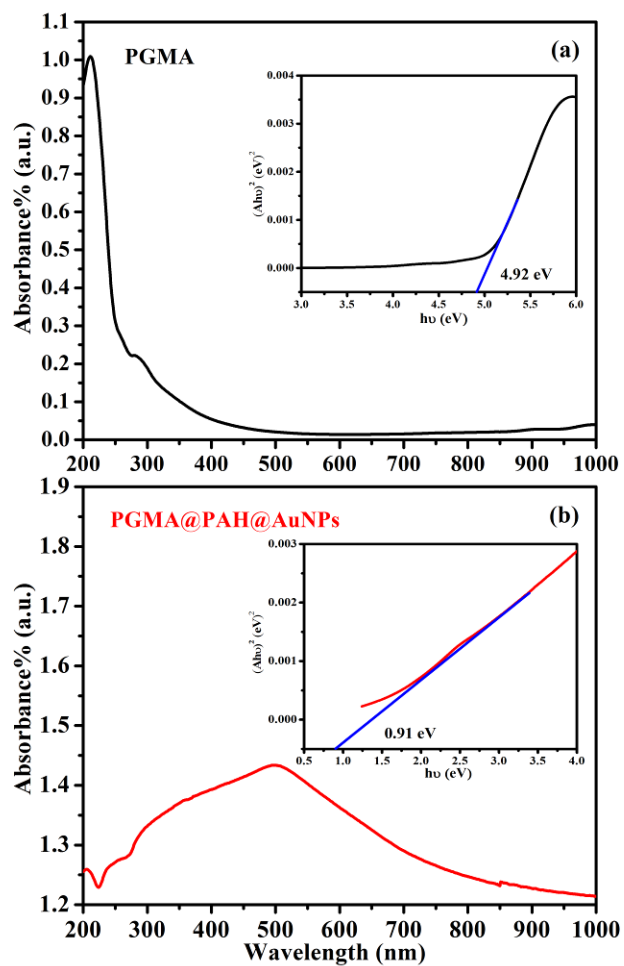


Figure 3-6. UV-vis absorbance spectra (converted from diffuse reflectance spectra data) of (a) PGMA and (b) PGMA@PAH@AuNPs spheres, respectively. The insets show the plots to obtain the band gap for a direct band gap transition for (a) and (b).

state must be partially filled; otherwise, when fully filled with electrons, it is inert to block the passage of other electrons via that state. The discontinuous gold nanoparticle network provides appropriate partially filled states and state delocalization to form a lower band gap.

3.4. Conclusions

In summary, negatively charged crystalline gold nanoparticles were successfully coated on the chemically reactive PGMA sub-microspheres that were modified with a layer of positively charged PAH film by a readily controlled assembly method. With the comparison of the peak position and average crystallite size from XRD, PAH not only modified the surface of the PGMA particles but also positively affected the crystallite of the PGMA particles. Moreover, the thermal stability of the PGMA spheres was improved by introducing gold nanoparticles in both air and N₂ conditions. Gold nanoparticles coated on the PGMA sphere surface as a discontinuous structure have a significant effect on both dielectric and optical properties. The real permittivity of the PGMA@PAH@AuNPs composites is much higher than that of pure PGMA spheres, and with lower band gap value, the PGMA@PAH@AuNPs have a strong potential to expand the applications of polymer nanocomposites in sensors,^[69] semiconductive devices^[70] or catalysts.^[71]

3.5. References

- [1] J. G. McGrath, R. D. Bock, J. M. Cathcart, L. A. Lyon, *Chem. Mater.* **2007**, 19, 1584.
- [2] M. Honda, K. Kataoka, T. Seki, Y. Takeoka, *Langmuir* **2009**, 25, 8349.
- [3] Z. Z. Gu, H. Uetsuka, K. Takahashi, R. Nakajima, H. Onishi, A. Fujishima, O. Sato, *Angew. Chem. Int. Ed.* **2003**, 42, 894.
- [4] H. Kawaguchi, *Prog. Polym. Sci.* **2000**, 25, 1171.
- [5] J. Ugelstad, P. Stenstad, L. Kilaas, W. Prestvik, R. Herje, A. Berge, E. Hornes, *Blood purif.* **1993**, 11, 349.
- [6] D. Horak, *Acta Polym.* **1996**, 47, 20.
- [7] B. Lange, F. Fleischhaker, R. Zentel, *Phys. Status Solidi A* **2007**, 204, 3618.
- [8] S. W. Choi, Y. C. Yeh, Y. Zhang, H. W. Sung, Y. Xia, *Small*, **2010**, 6, 1492.
- [9] V. Šmigol, F. e. Švec, K. Hosoya, Q. Wang, J. M. Fréchet, *Die Ange. Makromol.Chem.* **1992**, 195, 151.
- [10] E. Sudol, M. El-Aasser, J. Vanderhoff, *J. Polym. Sci., Part A: Polym. Chem.* **1986**, 24, 3499.
- [11] K. Mallick, Z. Wang, T. Pal, *J. Photochem. Photobiol., A* **2001**, 140, 75.
- [12] C. Tseng, Y. Lu, M. El-Aasser, J. Vanderhoff, *J. Polym. Sci., Part A: Polym. Chem.* **1986**, 24, 2995.
- [13] C. K. Ober, K. P. Lok, M. L. Hair, *J. Polym. Sci., Part C: Polym. Lett.* **1985**, 23, 103.
- [14] M. Okubo, J. Izumi, T. Hosotani, T. Yamashita, *Colloid. Polym. Sci.* **1997**, 275, 797.
- [15] M. Okubo, J. Izumi, *Colloids Surf., A* **1999**, 153, 297.
- [16] M. Senna, J. Lee, *Polym. Sci.* **1995**, 273, 76.
- [17] H.-M. Cheng, H.-C. Hsu, S.-L. Chen, W.-T. Wu, C.-C. Kao, L.-J. Lin, W.-F. Hsieh, *J. Cryst. Growth* **2005**, 277, 192.
- [18] Z. Luo, C. Zou, S. Syed, L. A. Syarbaini, G. Chen, *Colloid. Polym. Sci.* **2012**, 290, 141.
- [19] S. Sivakumar, V. Bansal, C. Cortez, S. F. Chong, A. N. Zelikin, F. Caruso, *Adv. Mater.* **2009**, 21, 1820.
- [20] X.-C. Xiao, L.-Y. Chu, W.-M. Chen, S. Wang, R. Xie, *Langmuir*, **2004**, 20, 5247.
- [21] M. Egen, R. Zentel, *Macromol. Chem. Phys.* **2004**, 205, 1479.
- [22] N. Preda, E. Matei, M. Enculescu, E. Rusen, A. Mocanu, B. Marculescu, I. Enculescu, *J. Polym. Res.* **2011**, 18, 25.
- [23] S. Wei, Q. Wang, J. Zhu, L. Sun, H. Lin, Z. Guo, *Nanoscale*, **2011**, 3, 4474.
- [24] J. Oh, J.-H. Lee, J. C. Koo, H. R. Choi, Y. Lee, T. Kim, N. D. Luong, J.-D. Nam, *J. Mater. Chem.* **2010**, 20, 9200.
- [25] J.-H. Lee, Y. Lee, J.-D. Nam, *Macromol. Rapid Commun.* **2009**, 30, 52.
- [26] P. Liu, *Colloids Surf., A* **2006**, 291, 155.
- [27] W. Fu, H. Yang, L. Chang, M. Li, H. Bala, Q. Yu, G. Zou, *Colloids Surf., A* **2005**, 262, 71.
- [28] S. F. Lascelles, S. P. Armes, *J. Mater. Chem.*, **1997**, 7, 1339.
- [29] J.-H. Lee, D. O. Kim, G.-S. Song, Y. Lee, S.-B. Jung, J.-D. Nam, *Macromol. Rapid Commun.* **2007**, 28, 634.
- [30] K. Ding, Y. Wang, L. Liu, L. Liu, X. Zhang, Z. Guo, *J. Appl. Electrochem.* **2013**, 43, 567.
- [31] M. Brust, D. Bethell, C. J. Kiely, D. J. Schiffrin, *Langmuir* **1998**, 14, 5425.
- [32] K. Akamatsu, M. Kimura, Y. Shibata, S.-i. Nakano, D. Miyoshi, H. Nawafune, N. Sugimoto, *Nano letters*, **2006**, 6, 491.
- [33] G. S. Huang, Y.-S. Chen, H.-W. Yeh, *Nano letters*, **2006**, 6, 2467.

- [34] R. Elghanian, J. J. Storhoff, R. C. Mucic, R. L. Letsinger, C. A. Mirkin, *Science*, **1997**, 277, 1078.
- [35] S. Y. Kim, S. H. Kwon, Y. D. Liu, J.-S. Lee, C.-Y. You, H. J. Choi, *J. Mater. Sci.* **2014**, 49, 1345.
- [36] L. Xu, P. Cui, D. Wang, C. Tang, L. Dong, C. Zhang, H. Duan, V. C. Yang, *J. Chromatogr. A* **2014**, 1323, 179.
- [37] Y. Liu, M. Li, G. Chen, *J. Mater. Chem. A* **2013**, 1, 930.
- [38] G. Frens, *Nature*, **1973**, 241, 20.
- [39] A. Patterson, *Phys. Rev.* **1939**, 56, 978.
- [40] C. Zhang, J. Zhang, B. Han, Y. Zhao, W. Li, *Green Chem.* 2008, 10, 1094.
- [41] P.-Y. Silvert, K. Tekaiia-Elhsissen, *Solid State Ionics* **1995**, 82, 53.
- [42] V. Pol, A. Gedanken, J. Calderon-Moreno, *Chem. Mater.* **2003**, 15, 1111.
- [43] Y. Chen, X. Gu, C.-G. Nie, Z.-Y. Jiang, Z.-X. Xie, C.-J. Lin, *Chem. Commun.* **2005**, 4181.
- [44] J. Liu, N. Feng, S. Chang, H. Kang, *Appl. Surf. Sci.* **2012**, 258, 6127-6135.
- [45] Y. Mao, K. K. Gleason, *Langmuir*, **2004**, 20, 2484.
- [46] F. Djouani, F. Herbst, M. M. Chehimi, K. Benzarti, *Constr. Constr. Build. Mater.* **2011**, 25, 424.
- [47] W. Chen, Y. Liu, C. Liu, *J. Appl. Polym. Sci.* **2013**, 130, 106.
- [48] L. G. Bach, M. R. Islam, D. C. Lee, K. T. Lim, *Appl. Surf. Sci.* **2013**, 283, 546.
- [49] X. Yan, Q. He, X. Zhang, H. Gu, H. Chen, Q. Wang, L. Sun, S. Wei, Z. Guo, *Macromol. Mater. Eng.* **2014**, 299, 485.
- [50] I. McNeill, *Eur. Polym. J.* **1970**, 6, 373.
- [51] I. McNeill, *Eur. Polym. J.* **1968**, 4, 21.
- [52] H. S. Nalwa, *Handbook of Low and High Dielectric Constant Materials and Their Applications, Two-Volume Set*, Academic Press, **1999**.
- [53] P. Barber, S. Balasubramanian, Y. Anguchamy, S. Gong, A. Wibowo, H. Gao, H. J. Ploehn, H.-C. Zur Loye, *Materials*, **2009**, 2, 1697.
- [54] Q. He, T. Yuan, J. Zhu, Z. Luo, N. Haldolaarachchige, L. Sun, A. Khasanov, Y. Li, D. P. Young, S. Wei, *Polymer*, **2012**, 53, 3642.
- [55] X. Huang, P. Jiang, C. Kim, F. Liu, Y. Yin, *Eur. Polym. J.* **2009**, 45, 377.
- [56] Z. M. Dang, Y. H. Lin, C. W. Nan, *Adv. Mater.* **2003**, 15, 1625.
- [57] K. Yang, X. Huang, Y. Huang, L. Xie, P. Jiang, *Chem. Mater.* **2013**.
- [58] Z.-Y. Shen, Y.-M. Li, W.-Q. Luo, Z.-M. Wang, X.-Y. Gu, R.-H. Liao, *J. Mater. Sci. - Mater. Electron.* **2013**, 24, 704.
- [59] A. Babel, D. Li, Y. Xia, S. A. Jenekhe, *Macromolecules*, **2005**, 38, 4705.
- [60] E. Yablonovitch, G. D. Cody, *Electron Devices, IEEE Trans.* **1982**, 29, 300.
- [61] G. L. Duveneck, J. Dbendorfer, R. E. Kunz, G. Kraus, Google Patents, **2002**.
- [62] P. K. Jain, K. S. Lee, I. H. El-Sayed, M. A. El-Sayed, *J. Phys. Chem. B* **2006**, 110, 7238.
- [63] K. L. Kelly, E. Coronado, L. L. Zhao, G. C. Schatz, *J. Phys. Chem. B* **2003**, 107, 668.
- [64] J. Tauc, *Mater. Res. Bull.* **1970**, 5, 721.
- [65] V. Senthamilselvi, K. Ravichandran, K. Saravanakumar, *J. Phys. Chem. Solids* **2012**.
- [66] J. Hou, H.-Y. Chen, S. Zhang, R. I. Chen, Y. Yang, Y. Wu, G. Li, *J. Am. Chem. Soc.* **2009**, 131, 15586.
- [67] A. M. Smith, S. Nie, *Acc. Chem. Res.* **2009**, 43, 190.
- [68] J. FAN, Y. M. MALOZOVSKY, *Int. J. Mod. Phys. B* **2013**.

- [69] H. Gu, J. Guo, H. Wei, Y. Huang, C. Zhao, Y. Li, Q. Wu, N. Haldolaarachchige, D. P. Young, S. Wei, *Phys. Chem. Chem. Phys.* 2013, 15, 10866.
- [70] H. Gu, J. Guo, S. Wei, Z. Guo, *J. Appl. Polym. Sci.*, 2013, 130, 2238.
- [71] K. Ding, H. Jia, S. Wei, Z. Guo, *Ind. Eng. Chem. Res.* 2011, 50, 7077.

**Chapter 4. An Innovative Method Applied to Synthesize Polymer Nanocomposites with a
Study of Different Temperature Effects on the Interface**

Abstract

Polypropylene (PP)/carbon nanotube (CNT) nanocomposites were prepared by coating CNTs onto the surface of gelated/swollen soft PP pellets. The electrical conductivity (σ) studies revealed a percolation threshold of only 0.3 wt%. At lower processing temperature, the CNTs formed a network structure more easily, resulting in a higher σ . The fraction of γ phase PP increased with increasing processing temperature. CNTs at lower loading (0.1 wt%) served as nucleating sites and promoted the crystallization of PP. CNTs favored the disentanglement of polymer chains and thus caused an even lower viscosity of nanocomposites than that of pure PP. The calculated optical band gap of CNTs was observed to increase with increasing processing temperature; i.e., 1.55 eV for nanocomposites prepared at 120 °C and 1.70 eV for those prepared at 160 and 180 °C. Both Drude model and interband transition phenomenon have been used for theoretical analysis of the real permittivity of the nanocomposites.

4.1. Introduction

The development of conductive or semi-conductive polymer nanocomposites (PNCs) has attracted much interest due to the unique physicochemical properties introduced into the otherwise inert hosting polymers, such as thermal stability,^[1-3] magnetic,^[4-7] optical,^[8-11] electrochromic^[12-14] and dielectric properties.^[15-17] Generally, the conductive PNCs have been prepared by introducing conductive nanofillers into the insulating polymer matrix. Among all the conductive nanofillers, carbon nanotubes (CNTs) show excellent physical properties, such as high aspect ratio (1000 for single walled CNTs)^[18] and great tensile strength and Young's modulus (63 and 950 GPa for the multi-walled CNTs (MWCNTs) respectively).^[19] Compared with metal nanofillers, CNTs with higher flexibility^[20] and lower density^[21] can enhance the mechanical, thermal and conductive properties of the polymers including polypropylene (PP).^[22] For instance, by limiting the crack propagation, the CNTs enhanced the yield stress and Young's modulus of PP.^[23] CNTs have also served as flame retardants. For example, the network layer of the MWCNT protected the inner PP layer by reducing the heat flux transmission.^[24] However, due to the poor dispersion of CNTs, a high CNT content is required to accomplish the conduction network in the polymer matrix.^[25] For instance, when PP was melt blended with MWCNTs, the electrical percolation threshold was achieved with a CNT loading between 1.0 and 2.0 wt%, and the volume resistivity of the PNCs with 5 wt% CNTs was still above 100 ohm·cm.^[26] The PP/MWNTs nanocomposites obtained by in-situ polymerization did not reach percolation even at a CNT loading of 3.5 wt% with a reported resistivity of about 1×10^{15} ohm·cm.^[27] Although a low percolation threshold of 0.097 vol% for the CNTs in polyester resin was reported from the rheological investigation,^[28] it would be more interesting to obtain the percolation threshold from the electrical conductivity to present the real percolating situation, considering the wrapping of polymer chains around the

CNTs to give a lower viscosity percolation value as observed in an epoxy nanosuspension with carbon nanofibers.^[29] To enhance the conductivity, additional treatments have been reported, including chemical functionalization with acid or amine, and heating. By immersing the MWCNTs in acid or octadecylamine solution, the MWCNTs were oxidized or grafted with amine groups, which improved the interfacial interaction between MWCNTs and the polymer matrix.^[30] Although annealing has removed amorphous carbon from MWCNTs,^[30] the electrical percolation threshold was achieved at a treated CNT loading between 1.0 and 2.0 wt% and the electrical conductivity of the PNCs with 5.0 wt% was still lower than 10^{-2} S/cm.^[30] However, these treatments would cause some negative effects on the conductivity of pristine CNTs by influencing the crystalline structure and interfacial characteristics^[31] or even introducing insulating layers.^[29] For instance, the partially damaged crystalline structure of the MWNTs from the treatment with concentrated HNO_3 and $\text{H}_2\text{O}_2/\text{NH}_4\text{OH}$ solution to introduce the carboxylic groups caused a lower conductivity.^[32]

Negative permittivity, normally observed in the negative refractive index, artificial-design, metal-based materials,^[33] was attributed to the plasma-like resonance of free electrons on the metal surface.^[34] For CNTs exhibiting a low plasma frequency, negative real permittivity can be observed when the test frequency was lower than the plasma frequency.^[35] The recently reported negative permittivity in the polyaniline- and polypyrrole-tungsten oxide^[36] and carbon nanofibers/elastomer PNCs,^[37] etc., were simply achieved by component incorporation rather than the traditional structure design. These materials have potential applications including cloaking, superlenses, wave filters, and superconductors.^[38-40] Although the optical and dielectric properties of pure CNTs have been studied due to their potential wide applications in energy storage^[41] and

electronic devices,^[42] few reports can be found on the optical and dielectric properties of the CNT reinforced PP PNCs, especially with a negative permittivity.

In this paper, PP nanocomposites with a unique structure were prepared by swelling the PP powders rather than dissolving them completely in the solvent to allow the surface of the PP powders to exhibit the gelate state for the CNTs to adhere to under an external shear force field. Then the dried PP powders wrapped with CNTs were hot pressed at 120, 160 and 180 °C to obtain the final nanocomposite finishing for tests. The melt rheological behaviors of the PNCs, including viscosity at steady state, viscosity storage and loss moduli and loss factor, were studied. For all the PNCs, the thermal stability was tested by TGA. The effects of CNTs on the crystalline structure of PP, including crystal structure, crystallization temperature, and crystalline fraction, were evaluated. The effects of both the CNT loading and the processing temperature on the optical property were studied by Taue plot and theoretically analyzed with the strain loaded on the CNTs in the PP matrix. The unique dielectric property of the PNCs was theoretically analyzed with the popular Drude model and interband transition phenomenon for the permittivity transitions between positive and negative.

4.2. Experimental

4.2.1 Materials

The polypropylene (PP) used in this study was supplied by Total Petrochemicals USA Inc. The carbon nanotubes (CNTs, SWeNT SMW100; average diameter: 6–10 nm; length: >1 μm; BET surface area: 300–330 m²/g) were provided by SouthWest NanoTechnologies, Inc. The solvent xylene (laboratory grade, $\rho=0.87$ g/cm³) was purchased from Fisher Scientific. All the chemicals were used as-received without any further treatments.

4.2.2 Preparation of PP/CNT Nanocomposites

The PP/CNTs nanocomposites with 0.1, 0.3, 1.6 and 2.0 wt% CNTs were prepared. Briefly, 20 g of PP powder were dispersed in 200 mL xylene and magnetically stirred at 70 °C for 24 hours to allow the PP powder to swell completely. When the surface of the swollen PP pellet was in the gelate phase and became very soft, the CNTs were added to the solution and the mixture was further stirred for 12 hours. The CNT loading in the PNCs was controlled by varying the weight of CNTs added into the above solution. Finally, extra xylene was vaporized and the PP powder coated with CNTs were obtained. The final powders were hot pressed under the pressure of 1 PSI for 30 min to form a round disk for testing. Three temperatures of 120, 160 and 180 °C were selected to study the effect of processing temperature on the physical properties of the PNCs.

4.2.3 Characterization

Rheological Behavior of PP/CNT Nanocomposite Melts: The rheological melt behavior of the nanocomposites was investigated with a rheometer (AR 2000ex, TA Instruments). An environmental test chamber (ETC) in a steel parallel-plate geometry (25 mm in diameter) was used to perform the measurements at shear rates ranging from 0.1 to 100 1/s at 200 °C. The samples were loaded into the model when the temperature was heated to 200 °C. Dynamic rheological measurements were also performed with dynamic oscillation frequency ranging from 0.1 to 100 rad/s at a low strain (1.0 %), which was justified to be within the linear viscoelastic (LVE) range for these materials. The LVE range was determined by the strain-storage modulus (G') curve within the strain range from 0.01 to 100 at a frequency of 1 rad/s.

Crystalline Structure of the PP/CNT Nanocomposites: The crystalline structure of pure PP and its PNCs was studied by X-ray diffraction (XRD), which was carried out using a Bruker AXS

D8 Discover diffractometer operating with a Cu K α radiation source ($\lambda=0.154\text{nm}$). The X-ray was generated at 40 kV and 27 mA power and the scans were recorded at 2θ from 5 to 30°.

Thermal Characterization of PP/CNT Nanocomposites: The thermal stability of the PP/CNT PNCs was studied by a thermogravimetric analysis (TGA, Q500, TA Instruments). All the samples were heated from 30 to 600 °C with a nitrogen flow rate of 60 mL/min and a heating rate of 10 °C/min. Differential scanning calorimetry (DSC, TA Instruments Q2000) measurements were implemented under a nitrogen flow rate of approximately 20 mL/min at a heating rate of 10 °C/min. The specimens were first heated from room temperature to 200 °C to remove the effect of the previous thermal history, and then cooled down to room temperature; after that the specimens were reheated again from room temperature to 200 °C.

Morphological Characterizations of PP/CNT Nanocomposites: The hot pressed samples were broken in liquid nitrogen and the morphology of the fracture surface of the samples was characterized with a field emission scanning electron microscope (SEM, JEOL JSM-6700F). The dispersion of the CNTs in the PNCs was studied by transmission electron microscope (TEM, JEOL JEM-2010 FastEM) with an accelerating voltage of 200 kV. The PP/CNT nanocomposites were cut into thin strips and embedded into epoxy capsules, which were cured at 60 °C for 24 hours. Then, the samples were microtomed into ca. 70 nm thick slices using an Ultra 45° diamond knife. The slices were deposited onto 400 mesh copper grids for imaging.

Optical Properties of PNCs: The UV-vis-NIR diffuse reflectance spectra (DRS) of the PP/CNTs PNCs were recorded on a JASCO spectrophotometer (Model V-670) equipped with a Jasco ISN-723 diffuse reflectance accessory. The PP/CNT samples used for the test were molded

by hot pressing the composite powders at 120, 160 and 180 °C into a cylindrical shape with 25 mm diameter and ~2.0 mm thickness.

Electrical Conductivity and Dielectric Permittivity Measurements: The electrical conductivity was measured following a standard four probe method. To make sure that a precise voltage was applied on the two inner probes, the V-source testing mode (Keithley 2400 source meter USA) was introduced. The measured voltage was adjusted in the range of -1 to 1 V and the corresponding current was measured and recorded across the two outer probes. The dielectric permittivity was measured by a LCR meter (Agilent, E 4980A) equipped with a dielectric test fixture (Agilent, 16451B) at the frequency of 20-2M Hz. A piece of rectangular standard Teflon sample with a permittivity of 2.1-2.4 was used for calibration before each test. The samples for both tests were prepared under the same procedures as that for the optical property test.

4.3. Result and discussion

4.3.1 Melt Rheological Behaviors of PP/CNT PNCs

The rheological behavior was tested for the melts at 200 °C of pure PP and its CNT nanocomposites processed at different temperatures. Both Newtonian and shear thinning behavior were observed for the melts of pure PP and its PNCs. As shown in Figure 4-1, for pure PP, the first Newtonian plateau with a constant viscosity is clearly observed, at which stage the rebuilding of polymer chain entanglement network can follow the rate of breaking of the physical cross-link sites.^[43] However, with increasing the shear rate, the rebuilding rate becomes lower than that of the physical cross-link breaking rate.^[43] The viscosity begins to sharply decrease and the polymer melt enters a shear thinning region. For pure PP, the shear thinning region manifests when the shear rate is increased to higher than 5 s^{-1} ; however, for the PNCs, the shear thinning behavior can be observed at a much lower shear rate (0.1 s^{-1} in Figure 4-1(B-d)). The shift of shear

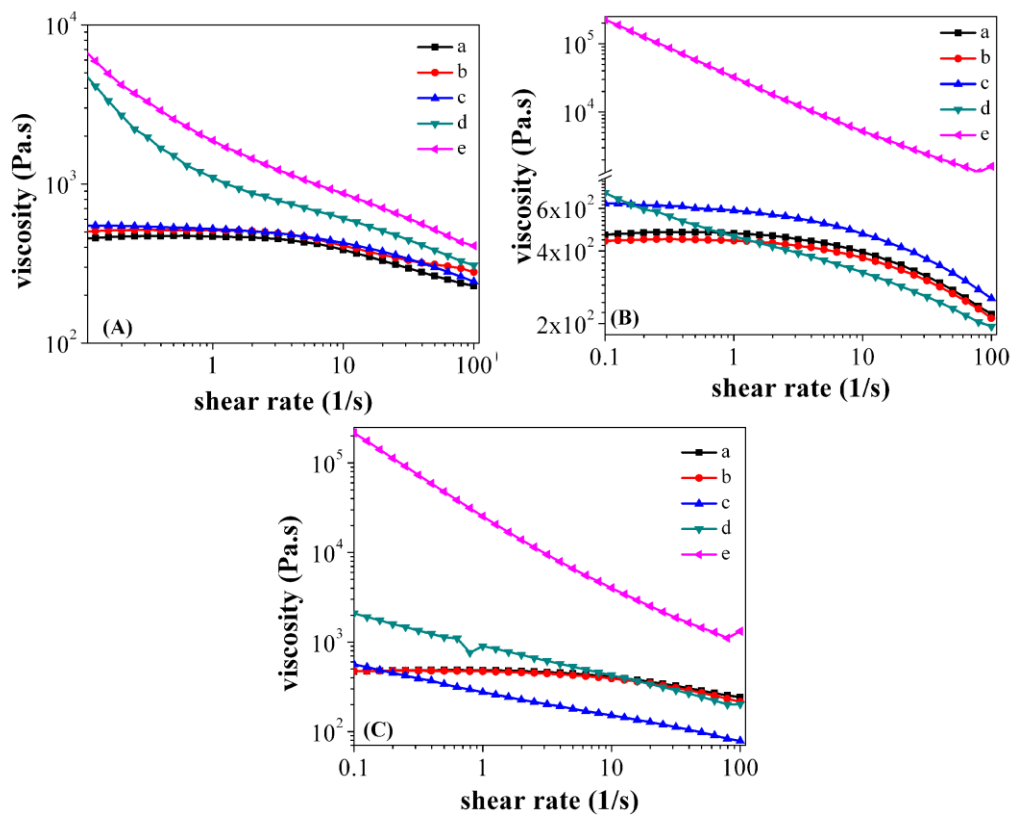


Figure 4-1. Viscosity vs. shear rate of (a) pure PP melt and its PNCs with the CNTs loading of (b) 0.1, (c) 0.3, (d) 1.6 and (e) 2.0 wt% processed at (A) 120, (B) 160 and (C) 180 °C.

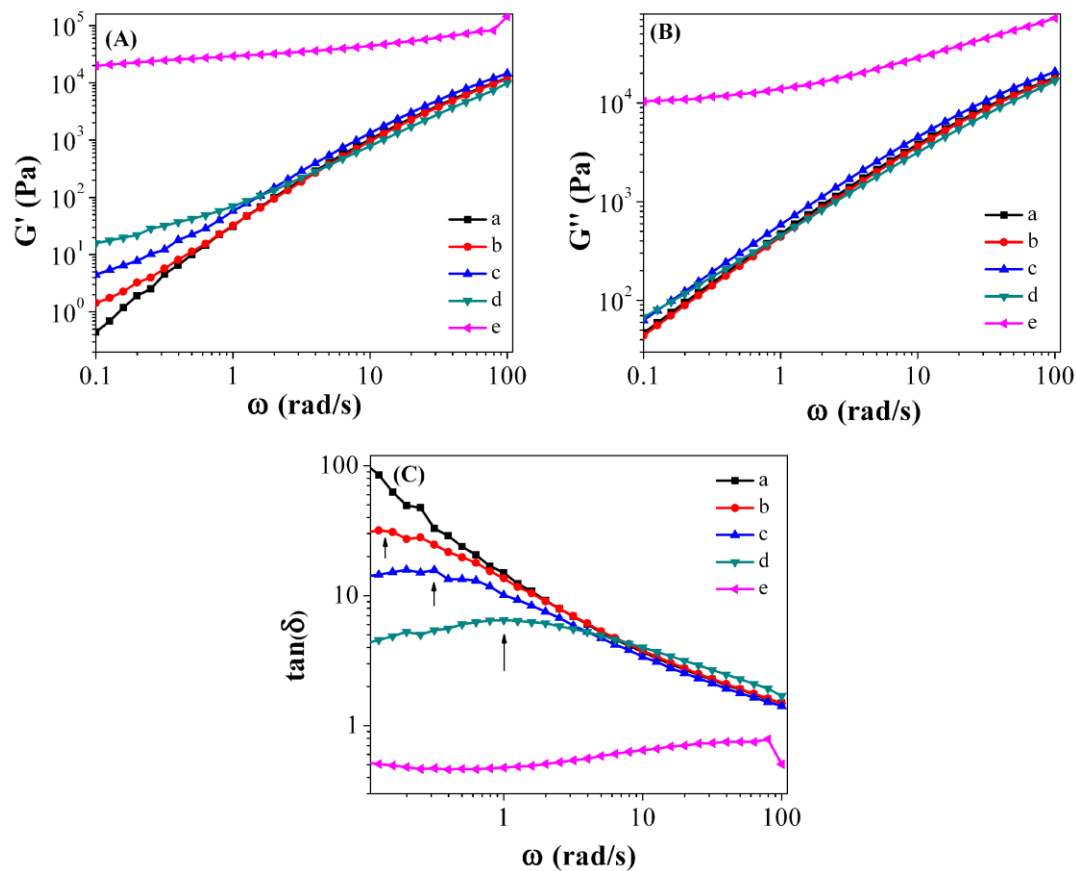
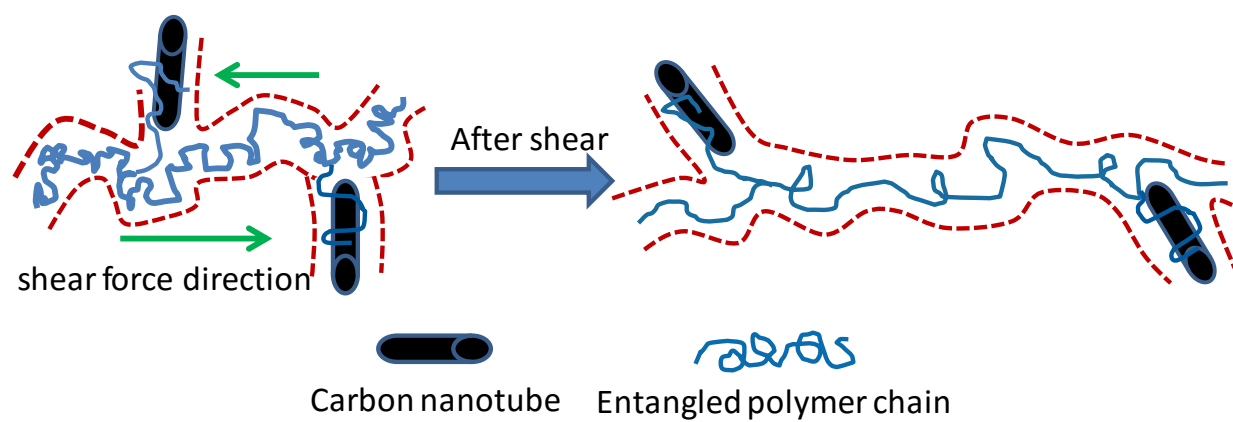


Figure 4-2. (A) Storage modulus (G'), (B) loss modulus (G'') and loss factor ($\tan\delta$) vs. angular frequency (ω) of (a) pure PP and its PNCs with the CNT loading of (b) 0.1, (c) 0.3, (d) 1.6 and (e) 2.0 wt%, processed at 160 °C.



Scheme 4-1. The nanoparticles act as branches of the PP polymer chain leading to an extensional force on the backbone.

thinning region to a lower shear rate range indicates that the CNTs favor the shear thinning behavior of the PP/CNT PNCs. The stronger shear thinning behavior was also observed in other nanocomposites,^[44, 45] for instance, layered double hydroxide/poly(ethylene terephthalate) and the nylon11/MWCNTs and was attributed to the orientation^[46] and the network structure breakdown of the nanofillers.^[47] Here, an increased pressing temperature leads to an improved dispersion of the CNT in the PP matrix, and the CNTs network would be much easier to destroy; thus, in the samples prepared at a higher pressing temperature, the shear thinning behavior was observed at a lower loading of CNT (Figure 4-1(B&C)).

It is worth noting that when shear thinning occurred, the viscosity of certain PNCs (1.0 wt% for 160 °C and 0.3 wt% for 180 °C) decreased even lower than that of pure PP. A decreased viscosity was also observed in the polymer nanosuspensions with nanoparticles.^[16, 48, 49] This unique phenomenon is related to two effects, one is the increased melt free volume resulting from the addition of nanoparticles in the entangled and confined systems ($h < R_g$, h is the average interparticle half-gap; R_g is the polymer radius of gyration),^[50, 51] the other is the dilution effect of nanoparticles, which provides a constraint release of polymer chain entanglement.^[50] However, unlike certain PNCs systems, such as the PP/alginate suspensions in which the viscosity is lower than that of bulk material in the whole test frequency range,^[52] in the PP/CNT system, the viscosity is higher than that of pure PP in the low shear rate range, and becomes lower than that of pure PP at higher shear rate (1.0 and 0.2 s^{-1} for Figure 4-1(B-d&C-c), respectively). A similar phenomenon was also observed in the study of long chain branching and linear materials, such as the metallocene polyethylenes with different long chain branching densities.^[53] Although the nanoparticles are reported to promote the orientation of polymer chains,^[54] only limited reports can be found on its mechanism. In the long chain branching material, the rheological behavior

would largely depend on reptation (a process by which a given chain crawls along the primitive path defined by topological constraints due to the other chains in the melt),^[55] the restraint of branches on the motion of backbone would lead to an extensional force on the backbone, which would further enhance the disentanglement of the polymer chains and caused a dramatically decreased viscosity.^[56] Thus, in the PP/CNT system, due to the interaction between nanofillers and the polymer matrix, the CNTs could serve as a branch of the polymer chains, which enhances the disentanglement^[57] under the shear field and causes a reduced viscosity (Scheme 4-1).

In addition, the storage modulus (G'), loss modulus (G'') and loss factor ($\tan\delta$) of the PP/CNT nanocomposites were also studied (Figure 4-2). Both G' and G'' increase with increasing the nanofiller loading in the low frequency range, which is also observed in the polylactide/layered silicate nanocomposite^[58] and is attributed to the enhanced solid-like behavior of the PNCs introduced by the nanofillers.^[59] The tendency of the solid-like behavior of the PNCs was also observed by the study of the $\tan\delta$ vs ω curve. As shown in Figure 4-2(C), with increasing the CNT loading, the peak of $\tan\delta$ shifts to a higher value. A switch from positive to negative for the slope of $\tan\delta$ indicates the transition of materials from solid-like to melt-like behavior.^[60] Thus, the peak shift of $\tan\delta$ also indicates the improvement of solid-like behavior of the PNCs. In addition, at low frequency, the “plateau” area is observed in both G' and G'' , where the G' and G'' values were less dependent on the frequency. The existence of a “plateau” area provides an indication of the interactions between the nanoparticles and the polymer matrix.^[61] Moreover, the value of loss $\tan\delta$ in PP was observed higher than that of PNCs; the increased $\tan\delta$ was attributed to the stronger interaction between the PP molecules and the CNTs than that among solely the PP molecules, which leads to more friction heat loss in pure PP than in the PNCs.^[62]

4.3.2 Crystalline Structure

The effects of processing temperature on the crystal structure of pure PP and its PNCs with 2.0 wt% CNTs were studied by XRD. As shown in Figure 4-3, for both pure PP and its PNCs prepared at 120 °C, the intensity of the first peak (110) is stronger than that of the second one (040), which is a typical XRD pattern of the α phase PP.^[61] The introduction of CNTs causes no variation of the crystal structure of PP resin for this temperature (Figure 4-3(A)). However, with the temperature increased to 160 and 180 °C, the characteristic peak of the γ phase at $2\theta = 20.07^\circ$ ^[61] was observed in both pure PP and its PNCs (Figure 4-3(B&C)). Meanwhile, the peak intensity at $2\theta = 18.50^\circ$,^[61] the distinctive peak of α phase PP, is decreased (Figures 4-3(B&C)). In order to explore the influence of CNTs on the crystalline phase of PP, the amount of γ phase PP (X_γ) is calculated by Equation (1).^[63]

$$X_\gamma = h_\gamma / (h_\gamma + h_\alpha) \quad (1)$$

where h_γ and h_α are the peak heights at $2\theta = 20.07$ and 18.5° for the (117) and (120) peaks, respectively. The value of X_γ was summarized in Table 4-1; it can be observed that compared with pure PP, the PNCs with 2.0 wt% CNT exhibit more γ phase PP, indicating that the CNTs promoted the γ phase PP formation. In addition, it is shown that for both pure PP and its PNCs, the percentage of γ phase PP increased with increasing the processing temperature and the γ phase PP became the dominant phase for the PNCs processed at 180 °C. The variation of the crystal structure was attributed to the higher crystallization temperature, which favors the γ phase PP formation.^[64]

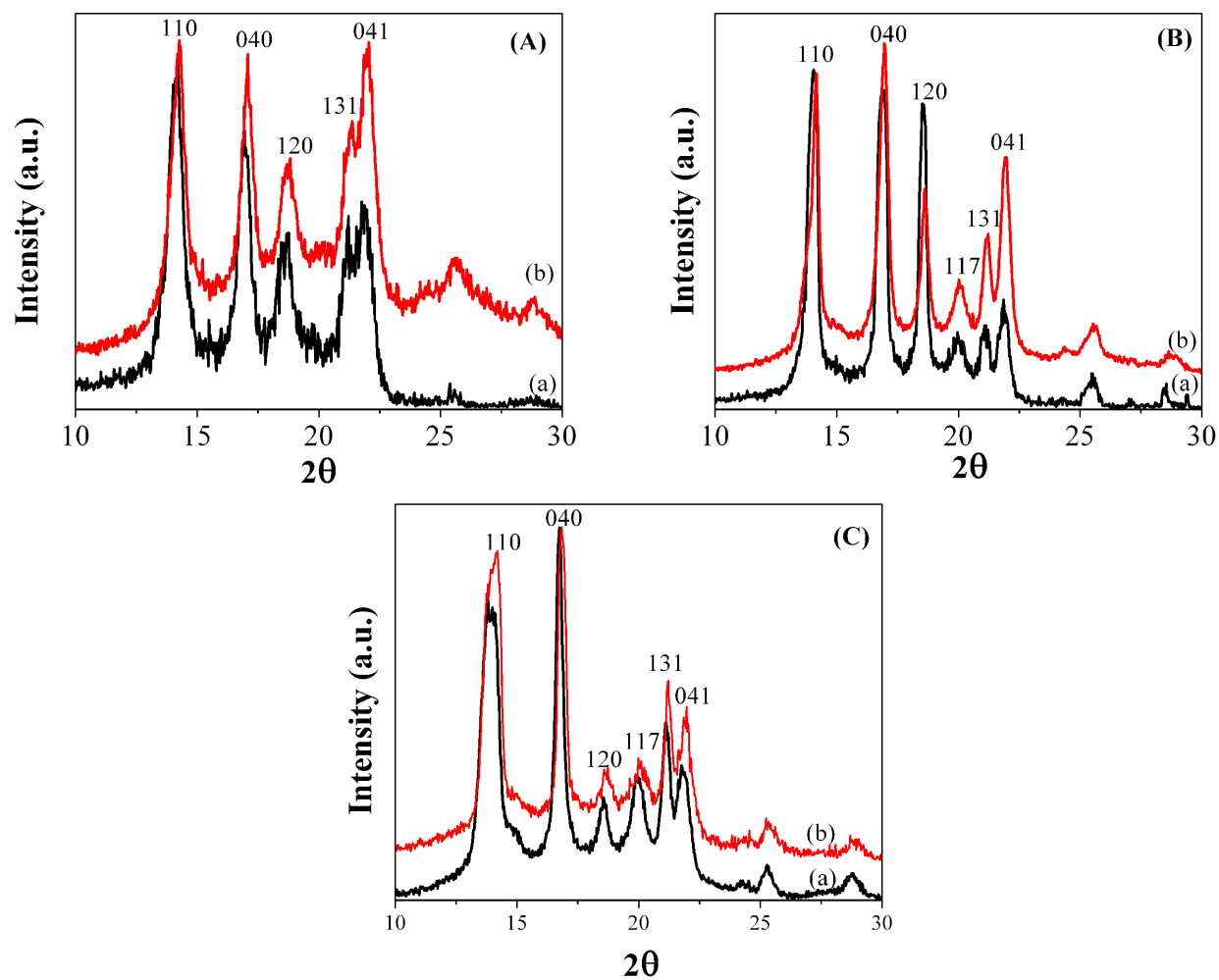


Figure 4-3. X-ray diffraction patterns of (a) pure PP and (b) its PNCs with 2.0 wt% CNTs processed at (A) 120, (B) 160 and (C) 180 °C.

Table 4-1. Amount of γ phase PP of pure PP and its PNCs with CNTs.

Samples	120 °C	160 °C	180 °C
Pure PP	0	0.1168	0.5770
2.0 wt% CNTs	0	0.2533	0.6276

4.3.3 Thermogravimetric Analysis of PP and its Nanocomposites

The thermal decomposition curves of pure PP and its CNT PNCs are shown in Figure 4-4. For all the samples, there is a sharp weight loss stage in the temperature range from 350 to 500 °C, which is caused by the chain break-down of the polymer structure. From the onset decomposition temperature (T_{1onset}) summarized in Table 4-2, the introduction of CNTs caused no obvious difference in the T_{1onset} value. However, after careful study of the DTG curves, an extra peak can be observed for all the PNCs between 300 to 400 °C, Figure 4-4(B). No peak is shown in the same range for both pure PP and pure CNTs, indicating that a new weight loss stage of the PNCs was introduced by the interaction between CNTs and PP. The onset decomposition temperature (T_{2onset}) of the weight loss stage from 300 to 400 °C was also summarized in Table 4-1. The T_{2onset} value was almost the same for all PNCs and did not change with increasing the CNT loading. This unique decomposition behavior of the PP/CNT PNCs in the low temperature range is probably due to the xylene wrapped within the PP matrix.^[65] Compared with the pure PP sample, it becomes more difficult to completely remove xylene in the PNCs due to the physical barrier effect of CNTs.

The crystallization and melting processes of pure PP and its PNCs were studied by the DSC test (Figure 4-5). The crystallization process can be observed in the DSC curve and the crystallization temperature (T_c) was summarized in Table 4-3. The value of T_c firstly increases with increasing the CNT loading, and then decreases with further increasing the CNT loading. The variation of T_c can be attributed to different functions of the CNTs during the crystallization of PP. The spherulitic growth rate (G) of the polymer crystallization can be expressed by Equation (2):

$$G = G_0 \exp \left[\frac{-U^*}{R(T_c - T_0)} \right] \exp \left[\frac{-K_g}{(T_c \Delta T f)} \right] \quad (2)$$

where G_0 is the pre-exponential factor, U^* is the activation energy for the transport of polymer chain segments to the crystallization sites, R is the gas constant, $\Delta T = T_m^0 - T_c$, where T_m^0 is the equilibrium T_m and T_c is the crystallization temperature, f is the factor representing the decrease in heat of fusion with decreasing temperature, T_0 is the hypothetical temperature where all the motions associated with viscous flow are prohibited and is usually taken 30K below the glass transition temperature,^[69] and K_g is the nucleation constant, which can be calculated based on Equation (3):^[67]

$$K_g = \frac{4EE_e b_0 T_m^0}{\Delta H_f k_B} \quad (3)$$

where E and E_e are side and fold surface free energies that represent the work required to create a new surface, b_0 is the single layer thickness, ΔH_f is the enthalpy of melting and k_B is the Boltzmann constant.

As shown in Equation (2), the crystallization formation is determined by two parts, the first part $\frac{-U^*}{R(T_c - T_0)}$ describes the transport of polymer chain segments to the growth front and the second part $\frac{-K_g}{(T_c \Delta T f)}$ is attributed to the nucleation process. The CNTs were reported serving as nucleation sites of PP^[70] The nucleation site could promote crystallization by reducing the surface free energy barrier (E, E_e) towards nucleation;^[71] thus for the PNCs with a lower loading (0.1

wt%) of CNTs, the crystallization of PP was initiated at a higher temperature than that of pure PP (Figure 4-5). However, with increasing the loading of CNTs, the nanofillers would constrain the movement of polymer chains to the growth front, leading to a higher U^* value and causing the crystallization temperature to shift to a lower value, which was also observed in the Fe@Fe₂O₃/PP PNCs.^[61]

In addition, it is worth noting the small shoulder observed in the PNCs with 2.0 wt% CNTs. It is known that the separation of the crystallization peak indicates a variation of the crystal structure. For pure PP with both α and the γ phases formed during crystallization, γ phase would firstly form dominant lamellae and the α phase would grow on it during the cooling process.^[72] Thus, the small shoulder can be attributed to the formation of the γ phase PP and the CNTs promote the γ phase PP, consistent with the XRD study.

For the second heating process, the melting peak was shown and the peak temperatures (T_m) were summarized in Table 4-3. The T_m of the PNCs was observed to be almost the same as that of pure PP. Both the enthalpies of fusion (ΔH_m) and crystallization (ΔH_c) were also summarized in Table 4-3. For all the samples, the value of ΔH_m was larger than ΔH_c , which was caused by the recrystallization of the samples. The crystalline fraction (F_c) of pure PP and its PNCs is calculated from Equation (4):^[73]

$$F_c = \frac{\Delta H_m}{\Delta H_m^0 f_p} \quad (4)$$

where ΔH_m is the enthalpy of the samples, and ΔH_m^0 is the enthalpy for a theoretically 100% crystalline PP (209 J/g)^[61] and f_p is the weight fraction of the polymer. From the results

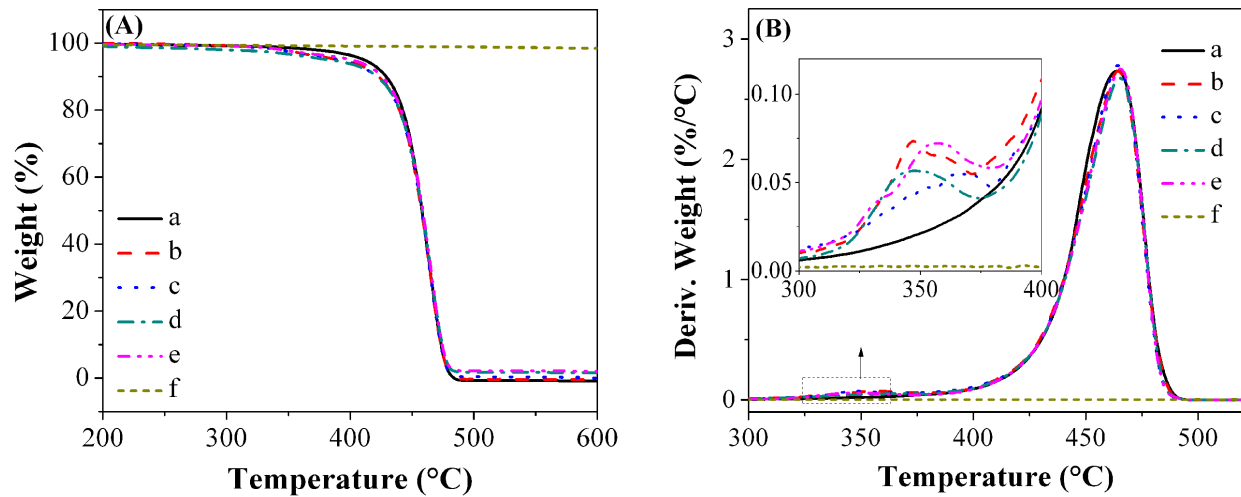


Figure 4-4. (A) Thermogravimetric analysis (TGA) curves and (B) derivative thermogravimetric (DTG) curve of (a) pure PP and its PNCs with the CNT loading of (b) 0.1, (c) 0.3, (d) 1.6 and (e) 2.0 wt%, and (f) pure CNTs.

Table 4-2. Onset temperature $T_{1\text{onset}}$ and $T_{2\text{onset}}$ of the pure PP and its PNCs with CNTs.

Samples	$T_{1\text{onset}}$ (°C)	$T_{2\text{onset}}$ (°C)
Pure PP	439.87	N/A
0.1 wt% CNTs	439.47	324.77
0.3 wt% CNTs	440.16	325.78
1.6 wt% CNTs	440.65	324.75
2.0 wt% CNTs	440.87	326.67

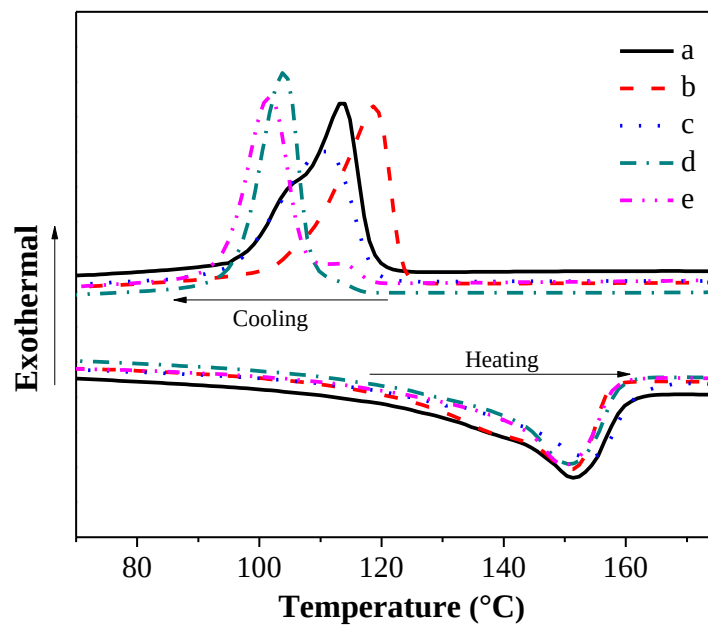


Figure 4-5. DSC curves of pure (a) pure PP and its PNCs with a CNT loading of (b) 0.1, (c) 0.3, (d) 1.6 and (e) 2.0 wt%.

Table 4-3. DSC Characteristics of pure PP and its PNCs with CNTs.

Loading of CNTs	T_c (°C)	ΔH_c (J g ⁻¹)	T_m (°C)	ΔH_m (J g ⁻¹)	F_c (%)
Pure PP	113.55	88.32	151.55	99.38	47.55
0.1 wt% CNTs	118.64	86.19	150.80	94.35	45.19
0.3 wt% CNTs	111.45	82.68	153.46	86.58	41.55
1.6 wt% CNTs	103.89	82.96	150.94	86.89	41.99
2.0 wt% CNTs	101.59	77.41	149.82	85.06	41.36

summarized in Table 4-3, it can be observed that the PNCs show a lower F_c than pure PP, which can be attributed to the disturbing effect of nanofillers during the formation of the crystalline structure of PP polymer chains.^[61]

4.3.4 Electrical Conductivity (σ) of PP/CNT Nanocomposites

The conductivity of the PNCs as a function of the CNT loading at different processing temperatures was shown in Figure 4-6. The conductivity ($\sim 1 \times 10^{-9}$ S/cm) of pure PP was from the literature.^[74] The conductivity is observed to increase with increasing the CNT loading, and the PNCs with 2.0 wt% CNTs and prepared at 120 °C exhibit the highest conductivity of 0.16 S/cm, which is four orders of magnitude higher than that of the PP/CNT PNCs even with 5 wt% CNTs prepared by dispersing the CNTs in the PP matrix.^[22] The outstanding electrical conductivity was attributed to the unique network formation of CNTs in PP. At 120 °C, PP just began to melt when the fabricated PP powder coated with CNTs was pressed, the powder would only change shape without breaking the coating layer of the CNTs, at which condition the CNTs would be pressed together (Scheme 4-2). The morphology of the PNCs was studied (Figure 4-7&8). For the PNCs prepared at 120 °C, the surface of the deformed powder with a CNT coating can be observed (Figure 4-7(A)), and the CNTs agglomerate together to form the network structures (Figure 4-8(A&C)).

However for the PNCs prepared at 160 and 180 °C, since the matrix was melted, the surface became flatter and the CNT coating layer was separated by PP (Figure 4-7(F)). The CNTs were observed dispersing among the PP matrix to build the network structure (Figure 4-8(B&D)). The network structure was observed with only 0.3 wt% CNTs in PNCs prepared under both high

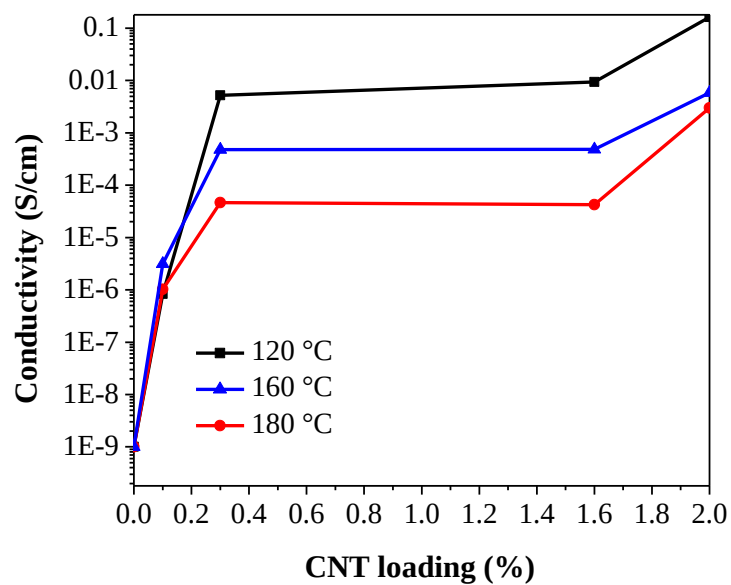


Figure 4-6. Electrical conductivity of PNCs vs CNT loading for the samples processed at (a) 120, (b) 160 and (c) 180 °C.

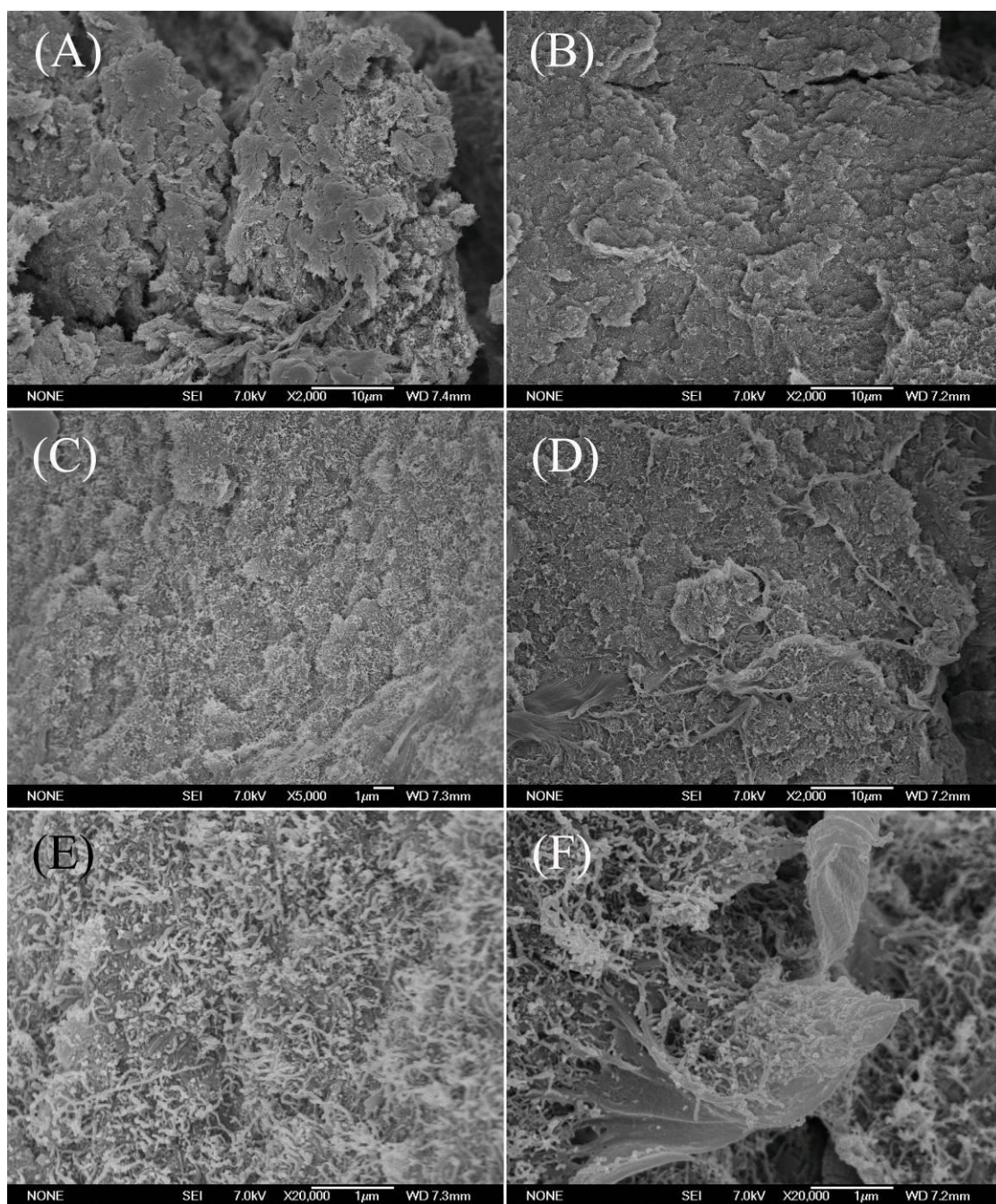


Figure 4-7. SEM microstructures of PNCs with 2.0 wt% CNTs prepared at (A) 120 °C and (B) 180 °C; PNCs with 0.3 wt% prepared at (C), (E) 160 °C and (D), (F) 180 °C.

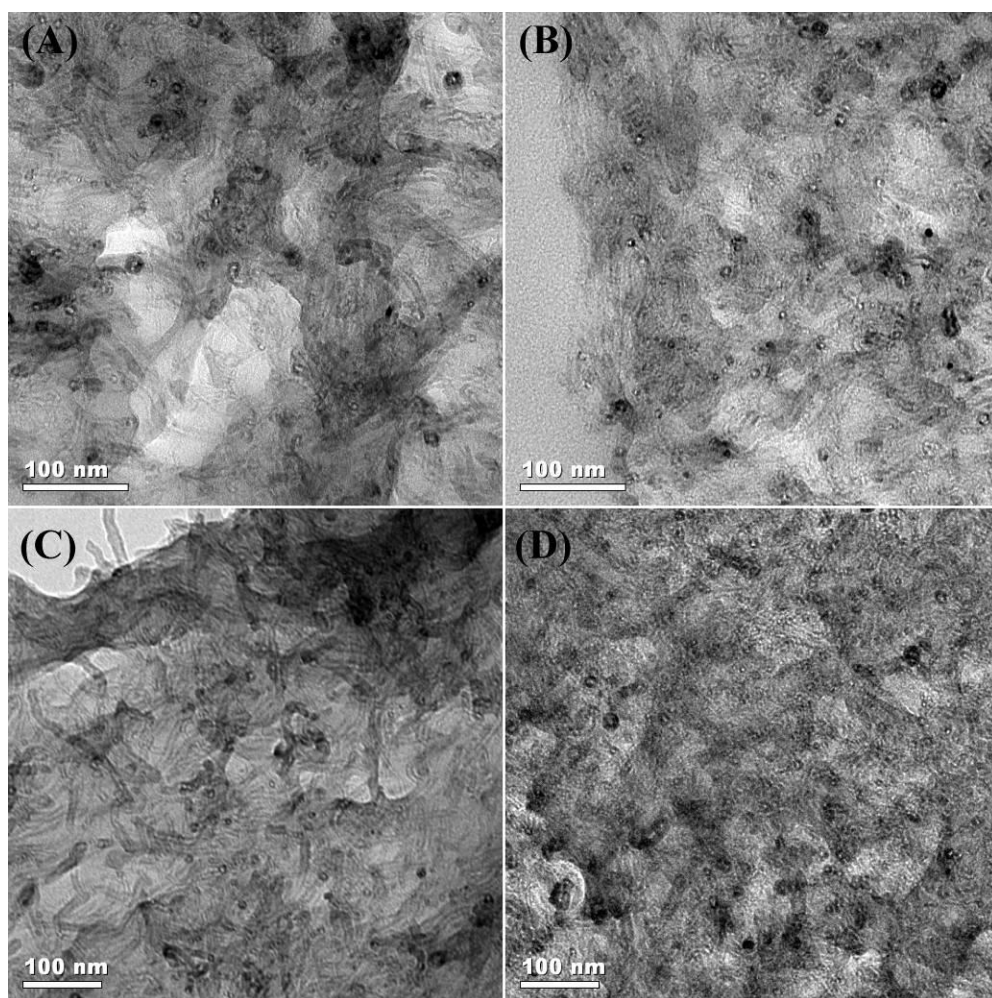
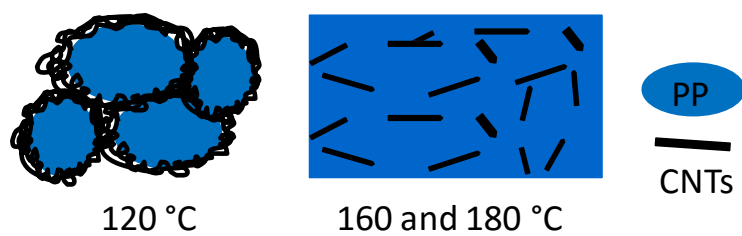


Figure 4-8. TEM microstructures of PNCs with 0.3 and 2.0 wt% CNTs prepared at (A, C) 120 °C and (B, D) 180 °C, respectively.



Scheme 4-2. The morphology of PNCs with CNTs at different processing temperatures.

(180 °C) and low (120 °C) temperatures, indicating the low percolation concentrations for all the PNCs.^[75] However, the network density is different. It is known that the conducting path was derived from the CNTs and at higher temperatures (160 and 180 °C), since the CNTs are dispersed within the PP matrix, limited CNTs can join in the conductive path formation.^[76] However, for the PNCs prepared at low temperature (120 °C), as the CNTs agglomerated to form the bundles, the network density increases. More CNTs are involved in forming the conductive network and lead to a higher electrical conductivity.^[76]

4.3.5 Optical Properties of PP/CNT Nanocomposites

The optical properties of pure CNTs and their PNCs were studied by ultraviolet-visible (UV-vis) spectroscopy (Figure 4-9). From the UV-vis absorbance spectra, the photonic energy band gap (E_g) value of the CNTs can be obtained from the Tauc plot,^[77] which describes the $\alpha h\nu$ value as a function of photon-energy ($h\nu$), Equation (5):

$$\alpha h\nu = (h\nu - E_g)^n \quad (5)$$

where α , h and ν are the absorbance coefficient, Planck constant, and photon frequency, respectively. The Tauc plot was converted from the diffuse reflectance UV-vis spectra. The parameter n is a pure number associated with the type of electronic transitions. n is 1/2 for the direct-allowed (characterized by the minimum energy level of the lowest conduction band positioned in k space directly under the maximum of the highest valence band) and is 2 for the indirect-allowed (instead of directly under the maximum of the highest valence band, the minimum energy level of the lowest conduction band is shifted relative to the maximum of the highest valence band in k space).^[78, 79] The value of n is reported to be 2^[80] for CNTs and the band gap value is obtained by the extrapolation of the linear portion of the curve to the energy axis. The

band gap of pure CNTs is found to be 1.50 eV (Figure 4-9 (B)), which is pretty close to the reported 1.543 eV for the transition between the second pair of van Hove singularity at above and below the Fermi level of CNTs with the assignment of (9,8).^[81]

The band gap (E_g^{opt}) values of pure CNTs and their CNT PNCs can be observed in Figure 4-9(B&D). The E_g^{opt} of all the PNCs is higher than that of pure CNTs, and decreases with increasing the CNT loading. At the same loading of CNTs, the E_g^{opt} of the nanocomposites depends on the processing temperature. The variation of E_g^{opt} can be attributed to the strain of CNTs,^[82] which was introduced during the hot pressing process. It is known that the band gap of CNTs depends on the diameter^[83] and chirality, which could vary with an applied strain.^[82] For CNTs, their chirality is defined by the tube index (m,n). The armchair metallic CNTs (m=n), which are of high symmetry, are less sensitive to the tensile strain than the semiconducting CNTs (m-n≠3N, N is an integer) with lower symmetries. The effect of strain on the band gap of CNTs is complicated. The strain on CNTs can play a positive or negative effect on the electrical properties of CNTs. It is observed that uniaxial or torsional strain could cause the insulator-metal transition of the SMNTs, due to the change of quantum number.^[84, 85] However, for graphene, uniaxial strain caused the red shift of the 2D and G bands, and the shift was studied with the elongation of the carbon-carbon bonds, which would weaken the bonds and led to a decreased vibrational frequency.^[86] For the PNCs, the shift of band gap was also observed in the poly(methyl methacrylate) (PMMA)/CNT system, and the effects of load transfer, strain and interfacial adhesion were studied, and the peak splitting observed at a higher strain (0.8%) was attributed to the slip of nanotubes in the polymer matrix.^[87] For the PP/CNT system, a lower E_g^{opt} value,

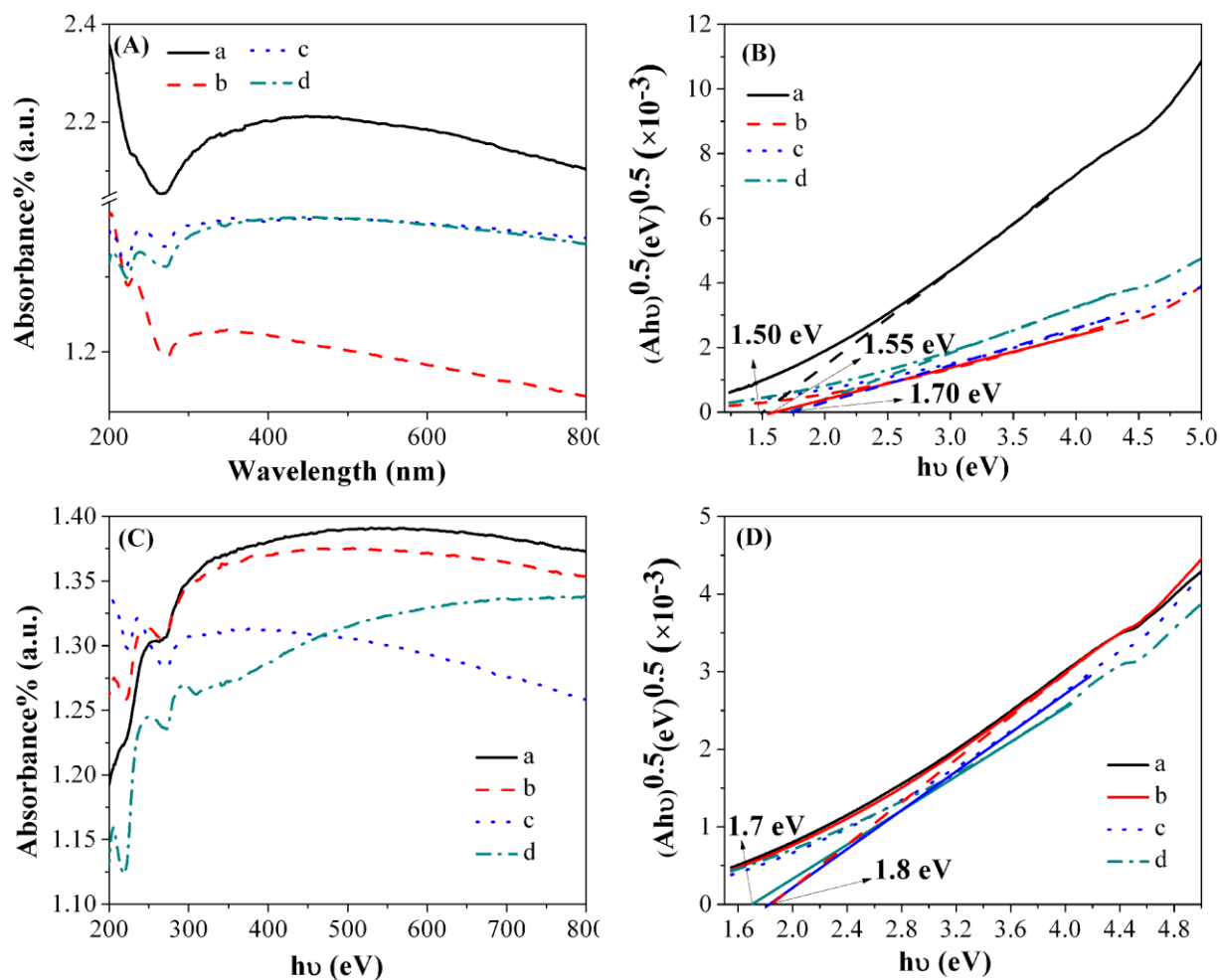


Figure 4-9. (A&C) Uv-Vis absorbance spectra and (B&D) converted from diffuse reflectance spectra data of (A&B) (a) pure CNTs and PNCs with 2.0 wt% CNTs processed at (b) 120, (c) 160 and (d) 180°C; (C&D) PNCs with the CNT loading of (a) 0.1, (b) 0.3, (c) 1.6 and (d) 2.0 wt%, processed at 160 °C.

Figure 4-9(B), was observed in the samples prepared at 160 and 180 °C, at which temperature, PP was already melted and the stronger deformation of polymer matrix would cause more strain on the CNTs. In addition, the changing trend of the E_g^{opt} value of the PNCs is consistent with the electrical conductivity of the PNCs; the PNCs with higher conductivity exhibit a lower E_g^{opt} .

4.3.6 Dielectric Permittivity

For the dielectric property study, the effects of processing temperature on the real permittivity (ϵ') of pure PP and its PNCs are shown in Figure 4-10. It is worth noting that the PNCs with 2.0 wt% CNTs processed at three different temperatures all exhibit processing temperature dependent negative ϵ' over the testing frequency range. The negative ϵ' is widely observed in the CNTs and is attributed to the metallic nature of the CNTs.^[35] However, the switching frequency from positive to negative depends on the composite sample pressing temperature. For the PNCs prepared at 120 °C, the negative ϵ' is observed at frequencies higher than 2000 Hz. However, the negative ϵ' is observed in the frequency range below 1000 Hz for the samples processed at 160 and 180 °C. In addition, it is worth noting that the variation tendency of the permittivity as a function of the frequency for the PNCs pressed at 120 °C (changing from positive to negative value with increasing frequency, Figure 4-10(A)) is in symmetry with that of PNCs pressed at 160 and 180 °C (changing from negative to positive value with increasing frequency, Figure 4-10(B&C)). The formation of the symmetric ϵ' variation trend was further explored by studying the relationship between the negative permittivity and the plasma frequency (ω_p). Negative permittivity observed in the metal-based negative refractive index materials^[33] was attributed to the plasma-like resonance of free electrons on the metal surface.^[34] The permittivity as a functional of ω_p was studied by Drude model, Equation (6):^[39]

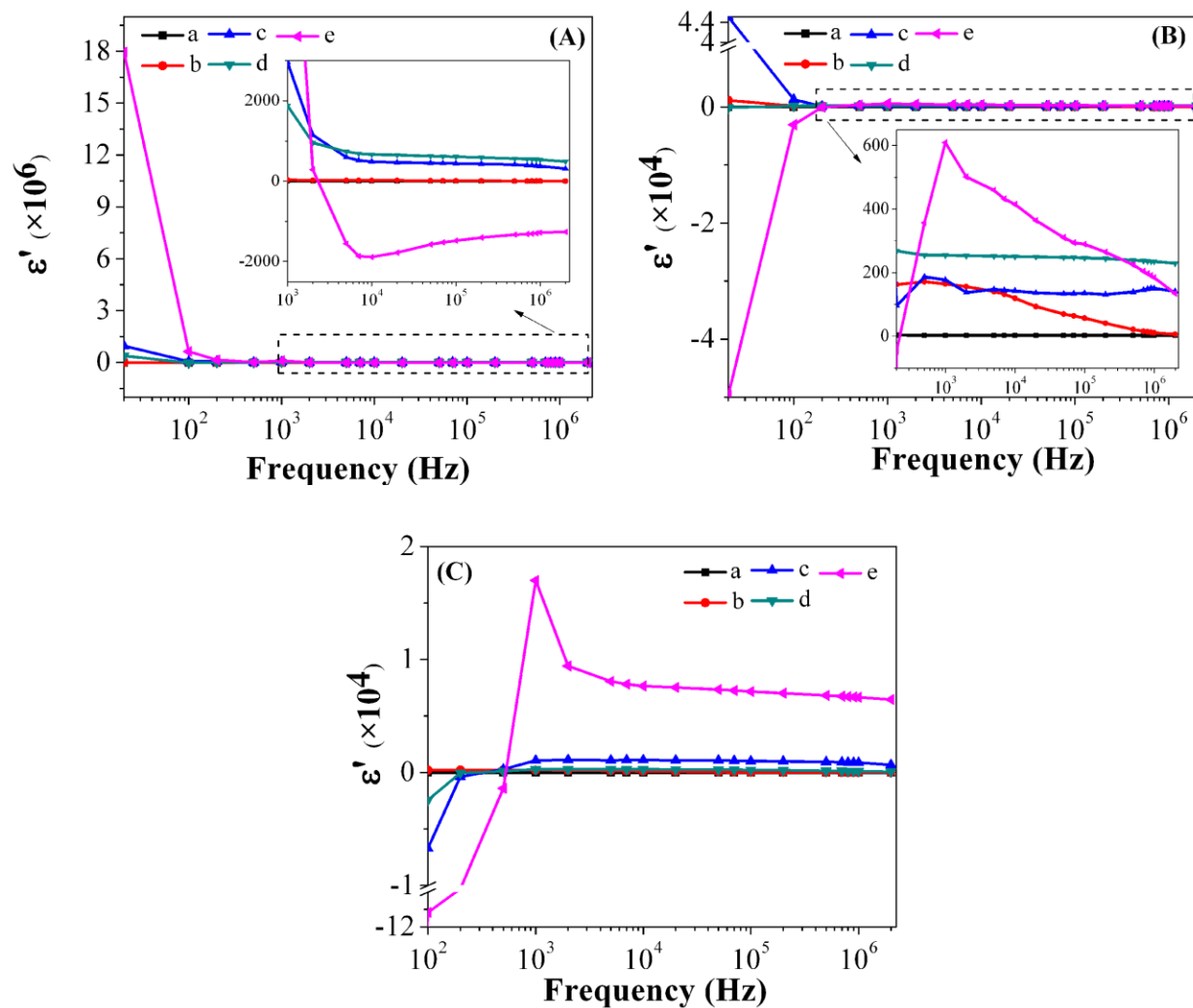


Figure 4-10. Real permittivity (ϵ') of (a) pure PP and its PNCs with the CNT loading of (b) 0.1, (c) 0.3, (d) 1.6 and (e) 2.0 wt%, processed at (A) 120, (B) 160 and (C) 180 °C.

$$\varepsilon^*(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i\gamma)} \quad (6)$$

where $\omega_p \equiv (Ne^2 / \varepsilon_0 m)^{1/2} = (4\pi Ne^2 / m^*)$ is the plasma frequency and m^* is the effective mass, γ stands for the damping constant, ε_0 is the vacuum permittivity, N represents the charge carrier density and ω is angular frequency.^[88] In order to fit the infrared optical data on the metals, the frequency dependent relaxation time is introduced to modify the Drude model (Equation (6)) to Equation (7):^[89, 90]

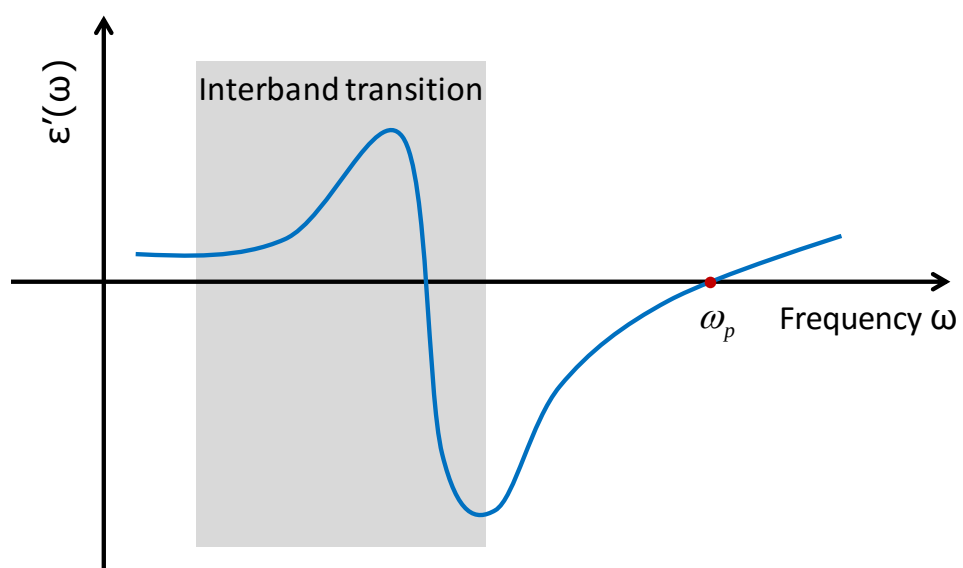
$$\varepsilon^*(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i\gamma)} = 1 - \frac{\omega_p^2}{\omega(\omega + i/\tau)} = \left(1 - \frac{\omega_p^2 \tau^2}{1 + \omega^2 \tau^2}\right) + i\left(\frac{\omega_p^2 \tau}{\omega(1 + \omega^2 \tau^2)}\right) \quad (7)$$

where τ is relaxation time and $\tau = 1/\gamma$. From Equation (7), negative permittivity is expected when the frequency is below the ω_p , and the permittivity becomes positive when the frequency is above ω_p .^[91] Based on Drude model, the ω_p values for the PNCs with 2.0 wt% CNTs processed at 160 and 180 °C should be between 200-1000 Hz considering the observed negative ε' at 200 Hz (below the ω_p) and positive ε' at 1000 Hz (above the ω_p), as in Figure 4-10(B&C). However, for the PNCs processed at 120 °C, Figure 4-10(A), ε' showed a positive value at a lower frequency and was decreased to negative values with increasing the frequency, which could not be described by the Drude model. The same phenomenon was also observed in polypyrrole (PPy),^[92] with the negative permittivity in the frequencies below the first ω_p changing to positive with frequencies above the first ω_p ; the ε' was decreased from positive to negative again with further increasing the frequency, ε' turned from negative to positive once more at the second ω_p . The first ω_p was

attributed to the most delocalized electrons, and the second ω_p originated from the confined electrons.^[92] In the study of negative permittivity in the metal materials, it was found that at wavelengths shorter than 550 nm, the Drude model was not accurate to describe the value of permittivity. In the low frequency range, the positive ϵ' would decrease and even turn to negative with increasing the test frequency. With further increasing the frequency, the variation of ϵ' would follow the Drude model.^[93] This unique variation of ϵ' as a function of frequency was known as an interband transition, as shown in Scheme 4-3. This interband transition can be attributed to the higher energy photons which promote electrons of lower-lying bands to the conduction band.^[93] When considering the interband transition, the Drude model can be written as Equation (8):^[93]

$$\epsilon_{interband}^*(\omega) = 1 + \frac{\omega_p^2(\omega_0^2 - \omega^2)\tau^2}{\omega^2 + (\omega_0^2 - \omega^2)\tau^2} + i \frac{\omega_p^2\omega\tau}{\omega^2 + \tau^2(\omega_0^2 - \omega^2)^2} \quad (8)$$

The interband transition has been observed in 2D graphene^[94] and PNCs with carbon nanofillers,^[95] where the second frequency for the variation of ϵ' from negative to positive was considered as ω_p .^[95] Here, for the PNCs with 2.0 wt% CNTs processed at 120 °C, Figure 4-10(A), the interband transition of ϵ' was observed to take place in a low frequency range (between 2000 and 5000 Hz); however, the ω_p for the variation of ϵ' from negative to positive was not observed. The lack of ω_p in the test frequency range was associated with the CNT network structure formed in the PNCs processed at 120 °C. It is known that the value of the ω_p depends on the 3-d network of the nanofiller in the polymer matrix.^[95] After dispersion in the polymer substrate, the dilution of the metallic wires would lead to a reduced density of the active electrons and thus the ω_p shifted to a lower frequency range.^[39] A similar phenomenon was also reported in the graphene nanocomposite



Scheme 4-3. Contribution of interband transition to the real permittivity as a function of frequency.

systems, where the ω_p was observed to depend on the carrier density in graphene.^[96] For the PNCs processed at 120 °C, the strong network of CNTs would lead to a high ω_p value, which exceeded the testing frequency range, thus, no ω_p was observed, Figure 4-10(A). In addition, since ω_p depends on the charge carrier density, the higher ω_p value of the PNCs processed at 120 °C indicates a higher charge carrier density; i.e., a higher electrical conductivity. This observed dielectric permittivity variation as a function of the processing temperature is in good agreement with the electrical conductivity study, in which the electrical conductivity of the PNCs processed at 120 °C is observed the higher than that of PNCs processed at 160 and 180 °C.

4.4. Conclusions

The CNTs coated on the surface of gelated/swollen soft PP powder were easily pressed together and formed a network structure in the hosting materials, which led to outstanding electrical properties. Meanwhile, the CNTs were observed to favor the formation of γ phase PP. The CNTs served as nucleating sites to promote the crystallization of PP at lower loading (0.1 wt%). CNTs also served as the branches of polymer chains to enhance the disentanglement of polymer chains and caused a decreased viscosity of PNCs even lower than that of pure PP. For the PP/CNT system, the lower band gap of the CNTs was associated with the stronger deformation of polymer matrix at elevated processing temperatures. Finally, the ω_p , which is proportional to the charge carrier density, was studied with the negative real permittivity observed in the PNCs. For the PNCs processed at 120 °C, the strong network of CNTs led to a high ω_p value and indicated a higher charge carrier density.

4.5. References

- [1] S. Stankovich, D. A. Dikin, G. H. B. Dommett, K. M. Kohlhaas, E. J. Zimney, E. A. Stach, R. D. Piner, S. T. Nguyen, R. S. Ruoff, *Nature* **2006**, 442, 282.
- [2] Q. Wang, J. Wu, Y. Gao, Z. Zhang, J. Wang, X. Zhang, X. Yan, A. Umar, Z. Guo, D. O'Hare, *RSC Advances*, 3, 26017.
- [3] Q. Wang, X. Zhang, C. J. Wang, J. Zhu, Z. Guo, D. O'Hare, *Journal of Materials Chemistry*, 22, 19113.
- [4] J. Gass, P. Poddar, J. Almand, S. Srinath, H. Srikanth, *Advanced Functional Materials* **2006**, 16, 71.
- [5] Q. He, T. Yuan, Z. Luo, N. Haldolaarachchige, D. P. Young, S. Wei, Z. Guo, *Chemical Communications* **2013**, 49, 2679.
- [6] H. Gu, S. Tadakamalla, Y. Huang, H. A. Colorado, Z. Luo, N. Haldolaarachchige, D. P. Young, S. Wei, Z. Guo, *ACS Applied Materials & Interfaces* **2012**, 4, 5613.
- [7] Q. He, T. Yuan, S. Wei, N. Haldolaarachchige, Z. Luo, D. P. Young, A. Khasanov, Z. Guo, *Angewandte Chemie International Edition* **2012**, 51, 8842.
- [8] X.-L. Xie, Y.-W. Mai, X.-P. Zhou, *Materials Science and Engineering: R: Reports* **2005**, 49, 89.
- [9] J. Jang, J. H. Oh, *Advanced Functional Materials* **2005**, 15, 494.
- [10] M. Chen, H. Qu, J. Zhu, Z. Luo, A. Khasanov, A. S. Kucknoor, N. Haldolaarachchige, D. P. Young, S. Wei, Z. Guo, *Polymer* **2012**, 53, 4501.
- [11] Z. Guo, S. Wei, B. Shedd, R. Scaffaro, T. Pereira, H. T. Hahn, *Journal of Materials Chemistry* **2007**, 17, 806.
- [12] H. Wei, X. Yan, S. Wu, Z. Luo, S. Wei, Z. Guo, *The Journal of Physical Chemistry C* **2012**, 116, 25052.
- [13] H. Wei, X. Yan, Y. Li, H. Gu, S. Wu, K. Ding, S. Wei, Z. Guo, *Journal of Physical Chemistry C* **2012**, 116, 16286.
- [14] J. Zhu, S. Wei, M. J. Alexander, T. D. Dang, T. C. Ho, Z. Guo, *Advanced Functional Materials* **2010**, 20, 3076.
- [15] Z. M. Dang, L. Wang, Y. Yin, Q. Zhang, Q. Q. Lei, *Advanced Materials* **2007**, 19, 852.
- [16] X. Zhang, Q. He, H. Gu, Z. Guo, S. Wei, *Journal of Materials Chemistry C* **2013**, 1, 2886.
- [17] H. Gu, Y. Huang, X. Zhang, Q. Wang, J. Zhu, L. Shao, N. Haldolaarachchige, D. P. Young, S. Wei, Z. Guo, *Polymer* **2012**, 53, 801.
- [18] M. J. Biercuk, M. C. Llaguno, M. Radosavljevic, J. K. Hyun, A. T. Johnson, J. E. Fischer, *Applied Physics Letters* **2002**, 80, 2767.
- [19] M.-F. Yu, O. Lourie, M. J. Dyer, K. Moloni, T. F. Kelly, R. S. Ruoff, "Strength and Breaking Mechanism of Multiwalled Carbon Nanotubes Under Tensile Load", 2000, p. 287/637.
- [20] S. Iijima, C. Brabec, A. Maiti, J. Bernholc, "Structural flexibility of carbon nanotubes", 1996, p. 104/2089.
- [21] M. Moniruzzaman, K. I. Winey, *Macromolecules* **2006**, 39, 5194.
- [22] Y. Li, J. Zhu, S. Wei, J. Ryu, Q. Wang, L. Sun, Z. Guo, *Macromolecular Chemistry and Physics* **2011**, 212, 2429.
- [23] K. Prashantha, J. Soulestin, M. F. Lacrampe, P. Krawczak, G. Dupin, M. Claes, *Composites Science and Technology* **2009**, 69, 1756.

- [24] T. Kashiwagi, E. Grulke, J. Hilding, K. Groth, R. Harris, K. Butler, J. Shields, S. Kharchenko, J. Douglas, *Polymer* **2004**, *45*, 4227.
- [25] J. Li, P. C. Ma, W. S. Chow, C. K. To, B. Z. Tang, J. K. Kim, *Advanced Functional Materials* **2007**, *17*, 3207.
- [26] M.-K. Seo, S.-J. Park, *Chemical Physics Letters* **2004**, *395*, 44.
- [27] A. A. Koval'chuk, A. N. Shchegolikhin, V. G. Shevchenko, P. M. Nedorezova, A. N. Klyamkina, A. M. Aladyshev, *Macromolecules* **2008**, *41*, 3149.
- [28] E. E. Ureña-Benavides, M. J. Kayatin, V. A. Davis, *Macromolecules*, *46*, 1642.
- [29] J. Zhu, S. Wei, A. Yadav, Z. Guo, *Polymer* **2010**, *51*, 2643.
- [30] S. H. Lee, E. Cho, S. H. Jeon, J. R. Youn, *Carbon* **2007**, *45*, 2810.
- [31] S. Bose, R. A. Khare, P. Moldenaers, *Polymer* **2010**, *51*, 975.
- [32] Y. J. Kim, T. S. Shin, H. D. Choi, J. H. Kwon, Y.-C. Chung, H. G. Yoon, *Carbon* **2005**, *43*, 23.
- [33] S. Zhang, W. Fan, N. C. Panoiu, K. J. Malloy, R. M. Osgood, S. R. J. Brueck, *Physical Review Letters* **2005**, *95*, 137404.
- [34] J. B. Pendry, L. Martı́n-Moreno, F. J. Garcia-Vidal, "Mimicking Surface Plasmons with Structured Surfaces", 2004, p. 305/847.
- [35] O. Hilt, H. B. Brom, M. Ahlskog, *Physical Review B* **2000**, *61*, R5129.
- [36] J. Zhu, S. Wei, L. Zhang, Y. Mao, J. Ryu, A. B. Karki, D. P. Young, Z. Guo, *Journal of Materials Chemistry* **2011**, *21*, 342.
- [37] J. Zhu, S. Wei, J. Ryu, Z. Guo, *The Journal of Physical Chemistry C* **2011**, *115*, 13215.
- [38] A. J. Hoffman, L. Alekseyev, S. S. Howard, K. J. Franz, D. Wasserman, V. A. Podolskiy, E. E. Narimanov, D. L. Sivco, C. Gmachl, *Nature material* **2007**, *6*, 946.
- [39] J. B. Pendry, A. J. Holden, W. J. Stewart, I. Youngs, *Physical Review Letters* **1996**, *76*, 4773.
- [40] O. V. Dolgov, D. A. Kirzhnits, E. G. Maksimov, *Reviews of Modern Physics* **1981**, *53*, 81.
- [41] R. H. Baughman, A. A. Zakhidov, W. A. de Heer, "Carbon Nanotubes--the Route Toward Applications", 2002, p. 297/787.
- [42] V. N. Popov, *Materials Science and Engineering: R: Reports* **2004**, *43*, 61.
- [43] M. Wang, W. Wang, T. Liu, W.-D. Zhang, *Composites Science and Technology* **2008**, *68*, 2498.
- [44] L. Sun, W.-J. Boo, J. Liu, A. Clearfield, H.-J. Sue, N. E. Verghese, H. Q. Pham, J. Bicerano, *Macromolecular Materials and Engineering* **2009**, *294*, 103.
- [45] L. Sun, J. Liu, S. R. Kirumakki, E. D. Schwerdtfeger, R. J. Howell, K. Al-Bahily, S. A. Miller, A. Clearfield, H.-J. Sue, *Chemistry of Materials* **2009**, *21*, 1154.
- [46] S. Huang, M. Wang, T. Liu, W.-D. Zhang, W. C. Tjiu, C. He, X. Lu, *Polymer Engineering & Science* **2009**, *49*, 1063.
- [47] W. D. Lee, S. S. Im, H.-M. Lim, K.-J. Kim, *Polymer* **2006**, *47*, 1364.
- [48] X. Zhang, O. Alloul, J. Zhu, Z. Luo, H. A. Colorado, N. Haldolaarachchige, D. P. Young, T. D. Shen, Q. He, S. Wei, Z. Guo, *RSC Advances* **2013**, 10.1039/C3RA41233D.
- [49] X. Zhang, Q. He, H. Gu, H. A. Colorado, S. Wei, Z. Guo, *ACS Applied Materials & Interfaces* **2013**, *5*, 898.
- [50] A. Tuteja, P. M. Duxbury, M. E. Mackay, *Macromolecules* **2007**, *40*, 9427.
- [51] S. Jain, J. G. P. Goossens, G. W. M. Peters, M. van Duin, P. J. Lemstra, *Soft Matter* **2008**, *4*, 1848.

- [52] T. Thanpitcha, Z. Li, R. Rujiravanit, A. Sirivat, A. Jamieson, *Rheologica Acta* **2011**, 50, 809.
- [53] D. Yan, W. J. Wang, S. Zhu, *Polymer* **1999**, 40, 1737.
- [54] E. Jaber, H. Luo, W. Li, D. Gersappe, *Soft Matter* **2011**, 7, 3852.
- [55] P. F. Green, P. J. Mills, C. J. Palmstr m, J. W. Mayer, E. J. Kramer, *Physical Review Letters* **1984**, 53, 2145.
- [56] R. A. Bubeck, *Materials Science and Engineering: R: Reports* **2002**, 39, 1.
- [57] S. S. Sternstein, A.-J. Zhu, *Macromolecules* **2002**, 35, 7262.
- [58] S. Sinha Ray, P. Maiti, M. Okamoto, K. Yamada, K. Ueda, *Macromolecules* **2002**, 35, 3104.
- [59] Y. H. Hyun, S. T. Lim, H. J. Choi, M. S. Jhon, *Macromolecules* **2001**, 34, 8084.
- [60] B. X. Fu, M. Y. Gelfer, B. S. Hsiao, S. Phillips, B. Viers, R. Blanski, P. Ruth, *Polymer* **2003**, 44, 1499.
- [61] J. Zhu, S. Wei, Y. Li, L. Sun, N. Haldolaarachchige, D. P. Young, C. Southworth, A. Khasanov, Z. Luo, Z. Guo, *Macromolecules* **2011**, 44, 4382.
- [62] X. Chen, S. Wei, A. Yadav, R. Patil, J. Zhu, R. Ximenes, L. Sun, Z. Guo, *Macromolecular Materials and Engineering*, 296, 434.
- [63] R. Thomann, C. Wang, J. r. Kressler, R. M hlhaupt, *Macromolecules* **1996**, 29, 8425.
- [64] K. Mezghani, P. J. Phillips, *Polymer* **1998**, 39, 3735.
- [65] P. a. Song, L. Liu, G. Huang, S. Fu, Y. Yu, Q. Guo, *Industrial & Engineering Chemistry Research* **2013**, 52, 14384.
- [66] J. D. Hoffman, R. L. Miller, H. Marand, D. B. Roitman, *Macromolecules* **1992**, 25, 2221.
- [67] G. Z. Papageorgiou, D. S. Achilias, D. N. Bikiaris, G. P. Karayannidis, *Thermochimica Acta* **2005**, 427, 117.
- [68] H. Tsuji, H. Takai, S. K. Saha, *Polymer* **2006**, 47, 3826.
- [69] S. Vyazovkin, J. Stone, N. Sbirrazzuoli, *Journal of Thermal Analysis and Calorimetry* **2005**, 80, 177.
- [70] B. P. Grady, F. Pompeo, R. L. Shambaugh, D. E. Resasco, *The Journal of Physical Chemistry B* **2002**, 106, 5852.
- [71] H. Li, M. A. Huneault, *Polymer* **2007**, 48, 6855.
- [72] T. Foresta, S. Piccarolo, G. Goldbeck-Wood, *Polymer* **2001**, 42, 1167.
- [73] Q. He, T. Yuan, X. Zhang, Z. Luo, N. Haldolaarachchige, L. Sun, D. P. Young, S. Wei, Z. Guo, *Macromolecules*, 46, 2357.
- [74] M.-K. Seo, J.-R. Lee, S.-J. Park, *Materials Science and Engineering: A* **2005**, 404, 79.
- [75] S. GD, L. DC, *J. Compos. Mater.* **2009**, 43, 917.
- [76] L. Hu, D. S. Hecht, G. Gr ner, *Nano Letters* **2004**, 4, 2513.
- [77] J. Tauc, *Materials Research Bulletin* **1970**, 5, 721.
- [78] A. Hjelm, C. G. Granqvist, J. M. Wills, *Physical Review B* **1996**, 54, 2436.
- [79] N. Serpone, D. Lawless, R. Khairutdinov, *The Journal of Physical Chemistry* **1995**, 99, 16646.
- [80] M. B. Tzolov, T.-F. Kuo, D. A. Straus, A. Yin, Xu, *The Journal of Physical Chemistry C* **2007**, 111, 5800.
- [81] G. Dukovic, F. Wang, D. Song, M. Y. Sfeir, T. F. Heinz, L. E. Brus, *Nano Letters* **2005**, 5, 2314.
- [82] E. D. Minot, Y. Yaish, V. Sazonova, J.-Y. Park, M. Brink, P. L. McEuen, *Physical Review Letters* **2003**, 90, 156401.

- [83] R. Martel, T. Schmidt, H. R. Shea, T. Hertel, P. Avouris, *Applied Physics Letters* **1998**, 73, 2447.
- [84] O. Gölseren, T. Yildirim, S. Ciraci, A. Kılıç, *Physical Review B* **2002**, 65, 155410.
- [85] L. Yang, M. P. Anantram, J. Han, J. P. Lu, *Physical Review B* **1999**, 60, 13874.
- [86] Z. H. Ni, T. Yu, Y. H. Lu, Y. Y. Wang, Y. P. Feng, Z. X. Shen, *ACS Nano* **2008**, 2, 2301.
- [87] T. K. Leeuw, D. A. Tsyboulski, P. N. Nikolaev, S. M. Bachilo, S. Arepalli, R. B. Weisman, *Nano Letters* **2008**, 8, 826.
- [88] M. Rashidi-Huyeh, B. Palpant, *Physical Review B* **2006**, 74, 075405.
- [89] S. R. Nagel, S. E. Schnatterly, *Physical Review B* **1974**, 9, 1299.
- [90] P. B. Johnson, R. W. Christy, *Physical Review B* **1972**, 6, 4370.
- [91] S. Enoch, G. Tayeb, P. Sabouroux, Guérin, Nicolas, P. Vincent, *Physical Review Letters* **2002**, 89, 213902.
- [92] R. S. Kohlman, J. Joo, Y. Z. Wang, J. P. Pouget, H. Kaneko, T. Ishiguro, A. J. Epstein, *Physical Review Letters* **1995**, 74, 773.
- [93] H. Lukas Novotny and Bert, L. a. B. H. Novotny, "Surface plasmons Principles of Nano-Optics", Cambridge University Press, 2006.
- [94] E. H. Hwang, S. Das Sarma, *Physical Review B* **2007**, 75, 205418.
- [95] B. Li, G. Sui, W.-H. Zhong, *Advanced Materials* **2009**, 21, 4176.
- [96] J. Zhu, Z. Luo, S. Wu, N. Haldolaarachchige, D. P. Young, S. Wei, Z. Guo, *Journal of Materials Chemistry* **2012**, 22, 835.

Chapter 5. Lowly Loaded Carbon Nanotube Induced High Electrical Conductivity and Large Magnetoresistance in Ethylene/1-Octene Copolymers

Abstract

High electrical conductivity in ethylene/1-octene copolymers (EOCs) was achieved by sticking CNTs onto the gelated EOC pellet surface and subsequent hot pressing. The electrical conductivity (σ) was observed to be dependent on the pressing temperature and the CNT loading. A variable range hopping (VRH) mechanistic study revealed a 3-d electron transport mechanism. Both unique positive and negative magnetoresistance (MR) phenomena were observed in these polymer nanocomposites (PNCs) and theoretically analyzed by two different models (a wave-function shrinkage model for positive GMR vs. a forward interference model for negative GMR). Other properties were tested and analyzed as well. Neat EOCs and their nanocomposites exhibited both Newtonian and shear thinning behaviors in the melt state. Less internal chain-chain friction heat was generated than that of neat EOCs after applying the same oscillation frequencies. The increased thermal stability of EOC nanocomposites was observed with increasing the CNT loading. An increased thermal conductivity (λ) was observed arising from the formed CNT network.

5.1. Introduction

Polymer nanocomposites (PNCs) attract increasing interest and demonstrate strikingly favorable performance arising from unique physicochemical properties including economical processability and low density of polymers, as well as functional merits of the nanofillers, including excellent mechanical strength and tunable magnetic, electric, optical and dielectric properties ^[1-4]. Among nanocomposites, conductive or semiconductive PNCs have captured growing interest arising from the introduced unique properties and potential usages, including energy storing units ^[5-7], sensing devices ^[8-10], kinesiology ^[11-13], fire retardants ^[14-16], microwave absorbers ^[17-19], and aerospace vehicles ^[20]. Ordinarily, conductive PNCs can be made by adding conductive nanofillers into insulative polymers. Among these reported conducting nanofillers, carbon nanotubes (CNTs) are highly flexible ^[21, 22], light-weight ^[23], and possess large aspect ratio (typically ca. 300-1000) ^[24], much higher tensile modulus (640 GPa to 1 TPa for single-walled CNTs (SWCNTs)) ^[25, 26], and outstanding electrical and thermal conductivities. Since the first report by Iijima in 1991 ^[27], and the first report of using CNTs as fillers by Ajayan in 1994 ^[5], CNTs have substituted or complemented conventional nanofillers for preparing multifunctional PNCs ^[28, 29]. The structural parameters can influence the properties of the CNTs, such as the electronic properties with the existing either metallic or semiconducting, and affect their applications. For example, CNTs can even serve as a flame retardant. The interconnecting MWCNTs significantly enhanced the thermal stability and reduced the heat release rate of polypropylene (PP) ^[30]. However, the surface inertness and large aspect ratio challenge their dispersion; therefore, a high loading was needed to form a conductive network ^[31]. For example, no percolation behavior was observed in the in-situ polymerized PP PNCs even at ~ 3.5 wt% CNTs loading ^[32]. To enhance the conductivity, aligned CNTs were explored with a narrow diameter

distribution and a given length by varying the production parameters^[33]. Furthermore, different functional groups have been introduced to make them interfacially compatible with the polymer^[34]. For instance, Barrau et al.^[35] treated MWCNTs with palmitic acid and the resulting epoxy PNCs showed enhanced electrical conductivity (σ) with improved dispersion of CNTs. However, these treatments could decrease the σ of pure CNTs with damaged crystalline structure^[36] and changed interfacial adhesion^[37]. For example, Gojny et al.^[38] reported a higher percolation threshold in the amino-functionalized CNTs than that in the pristine CNTs.

Block copolymers are produced by linking two or more chemically distinct polymer blocks^[39]. In the solid and rubbery states, copolymers have been used as thermoplastic elastomers offering combined characteristics of rubber and plastic^[40]. Copolymers of ethylene with α -olefins are now commercially available for wide applications^[41]. Ethylene/1-octene copolymers (EOCs) are the most important copolymers and can be used as good toughening modifiers for PP^[42, 43], polycarbonate (PC)^[44] and high density polyethylene (HDPE)^[45] because of their good thermal stability, weather resistance, excellent toughness, and aging resistance. Giant magnetoresistance (a resistance change larger than at least 1.0 % upon applying an external magnetic field) has been observed in multilayered metallic structures, carbon species, conductive polymers and their nanocomposites, and conductive epoxy nanocomposites with hybrid carbon nanofibers and nanomagnetite^[46-50]. However, the EOCs as the hosting polymer matrix for conductive PNCs have been rarely studied. The GMR and electron transport in the copolymer PNCs have been rarely reported either.

In the current study, EOCs with different CNT loading levels were prepared by a surface coating method. The EOCs pellets were swelled to allow CNTs to stick on their surface. The

preparation procedure was extremely mild, easy to control, and repeatable. Then the dried EOC pellets coated with CNTs were pressed at different temperatures to get the PNC final finishing. The morphology was investigated by SEM. The rheological behaviors of the nanocomposites in the melt state were investigated, including storage and loss moduli, steady state viscosity, and loss factor. The PNCs were studied by XRD, DSC, and TGA. The effects of CNT loading level and processing temperature on the electrical conductivity, optical properties, and thermal conductivity were investigated. The room-temperature resistance variation as a function of magnetic field (M-R) was recorded. The electron transport mechanism was investigated by the variable range hopping approach. Both positive and negative magnetoresistance were analyzed by using a wave-function shrinkage model and a forward interference model, respectively.

5.2. Experiments

5.2.1 Materials

The ethylene/1-octene copolymer (EOC) (Infuse 9500 Olefin Block Copolymer, Density: 0.878 g cm^{-3} , M_w : 82600 g mol^{-1} , M_w/M_n : 2.3, T_m : $122 \text{ }^\circ\text{C}$, T_g : $-45 \text{ }^\circ\text{C}$) used in this research was provided by Dow Chemical Company. The carbon nanotubes (CNTs, SWeNT SMW 200X) were supplied by SouthWest NanoTechnologies, Inc with a reported average diameter of 10.4 nm and average length of 4.3 μm . Laboratory grade xylene with a reported density (ρ) of 0.87 g cm^{-3} was purchased from Fisher Scientific and served as the solvent for the copolymers. No further treatment was made for all the chemicals before usage.

5.2.2 EOC-based nanocomposites: Preparation

The EOCs-nanocomposites with 0.7, 2.0, 3.6 and 6.8 wt% CNT loadings were prepared with a similar process as previously reported for PP nanocomposites^[29]. In short, the EOC powder

was dispersed first in xylene and magnetically stirred at 50 °C for 5 hours until the polymer powder was fully swelled. When the powder surface began to dissolve, the mixture was stirred for additional 5 hours after adding CNTs to the solution. Finally, EOC pellets coated with CNTs were obtained when extra xylene was vaporized. The final pellets were pressed into a round disk in a hot press for testing at 100, 120 and 160 °C to study the effects of processing temperature on the nanocomposites.

5.2.3 Characterizations

The rheological properties of the nanocomposites in the melt state were studied at shear rates varying from 0.01 to 10 s⁻¹ in a rheometer (AR 2000ex, TA Instruments) equipped with an environmental test chamber with a steel parallel-plate (25 mm in diameter) geometry to control the temperature at 170 °C. Dynamic rheological behavior was also measured at frequencies varying from 0.1 to 100 rad s⁻¹ at a low strain of 1.0 % (within the linear viscoelastic range). The strain-storage modulus (G') curve was used to determine the linear viscoelastic range with the strain changing from 0.1 to 100 and a constant frequency of one rad/s.

A Bruker AXS D8 Discover diffractometer was used to study the crystalline structure of pure EOC and its composites. A thermogravimetric analyzer (TGA, Q-500, TA Instruments) was used to evaluate the thermal stability at a 60 mL/min nitrogen flow rate and a heating rate of 10 °C/min. The evaluated temperature was adjusted from 30 to 600 °C. With a nitrogen flow rate of 20 mL/min and a heating rate of 10 °C/min, further testing was done using a differential scanning calorimeter (DSC, TA Instruments Q2000). The temperature was changed from room temperature to 180 °C to eliminate the thermomechanical effect. The temperature was then lowered to room temperature and reheated back to 180 °C.

The thermal conductivity was measured by utilizing a direct measuring device (LaserComp, FOX50), capable of testing samples from -10 to 110 °C. The measureable thermal conductivity range was from 0.1 to 100 W m⁻¹ K⁻¹. The samples were prepared following the requirements as designed by the ASTM C518. The specimen with flat parallel surfaces was placed between the top plate (hot surface) configured to be at a higher temperature and the bottom plate (cold surface) at lower temperature. Therefore, the heat flow went from the top to the bottom. The thickness of the specimen was measured by the equipment. Each sample was measured at an average temperature of 15, 25, 35, 45, 55, and 65 °C, respectively.

The morphology of the fracture surface was observed by a field emission scanning electron microscope (SEM, JEOL JSM-6700F). The samples were prepared by breaking the hot-pressed nanocomposite films in liquid nitrogen and coating with a thin gold coating before testing.

The UV-vis-NIR diffuse reflectance spectra (DRS) of the PNCs were recorded by A JASCO spectrophotometer (Model V-670) having a Jasco ISN-723 diffuse reflectance accessory. The samples were prepared in the same way as those for the resistivity test.

The EOC/CNT samples were pressed into a round shape film (2.0 mm thick) with a diameter of 25 mm under a pressure of 95 MPa in a hydraulic press. The standard four probe method was used to measure the electrical resistivity. Magnetoresistance (MR) at 130 and 290 K was obtained by measuring the resistance as a function of field with a standard four-probe technique in a 9-T Physical Properties Measurement System (PPMS, Quantum Design).

5.3. Results and Discussion

5.3.1 Melt Rheological Behavior

From processing and application aspects, the rheological behavior of PNCs melts is very important since it reflects the microstructure of materials, and the polymer-nanofiller interaction. Figure 5-1 presents the shear rate dependent viscosity of neat EOCs and their nanocomposite melts processed at different temperatures. Newtonian behavior was observed in all these samples together with the shear thinning (power law) behaviors under melting state. At a low shear rate, the alignment of CNTs was destroyed by random thermal motion. Meanwhile, the entanglement rebuilding of polymer chains can follow the speed of breaking the physical cross-linking. Therefore, the viscosity of PNCs is constant at low shear rates, and the region is called first Newtonian region ^[51]. However, the rebuilding rate becomes lower than that of breaking the physical cross-links with further increasing the shear rate, and a steady state alignment level is achieved. The viscosity would be reduced with increasing the shear rate, i.e., the shear thinning phenomenon was observed in the polymer melt. These curves clearly demonstrate a Newtonian phenomenon in the low shear rate region and a shear thinning phenomenon in the high shear rate region ^[52]. A constant viscosity plateau was observed indicating the Newtonian behavior of the neat EOCs and the viscosity began to decrease drastically at a shear rate larger than 1 s^{-1} , Figure 5-1. However, compared with the melt of neat EOCs, the sharp reduction positions of viscosity shift to lower shear rate for the PNCs (0.1 s^{-1} for 6.8 wt% CNTs, Figure 5-1c) with increasing the CNTs loading level, indicating that the nanotubes enhance the shear thinning behavior of the nanocomposites with different processing temperatures. At the same shear rate, the viscosity is increased with increasing the CNTs loading but is declined at 3.6 and 6.8 wt% CNTs. This

phenomenon can be clearly observed at higher shear rates and can be explained by the following two aspects. One is from the added nanofillers in the entangled and confined systems ($h < R_g$, h is the average half-gap between the particles; R_g is the polymeric gyration radius), which result in an increased melt free volume ^[53, 54]. Another reason is the nanoparticle dilution effect that provides constrained release of entangled polymer chains ^[53]. Other composites are also observed to show stronger thinning behavior. For example, Wang et al. ^[55] reported that polyamide 6/poly(ethylene-1-octene) (POE) blends displayed shear thinning behavior due to the diffusion of copolymers with POE chains to the PA6 matrix.

The formed percolated systems can be understood by studying the thermomechanical properties of the EOC/CNT nanocomposites melts processed at 140 °C as a function of frequency ^[56-58]. Figure 5-2a depicts the frequency dependent G' for pure EOC and nanocomposite melts measured at 170 °C. The observed fully relaxed EOC chains show a typical homopolymer-like terminal behavior and disappear with increasing the CNTs loading. The observed larger enhanced G' with orders of magnitude in the low frequency range indicates that the added CNTs restrained the relaxation of polymer chains at a large scale. Moreover, the G' curve of the PNCs with relatively higher CNT contents (≥ 2.0 wt%) reached a plateau in the low frequency range. This observed “plateau” represents either a strong particle-polymer interaction or an interconnected structure of fillers ^[57]. However, the influence of the CNT content on the rheological behavior is relatively weak in the high frequency range, demonstrating that the influence of the CNTs on the short-range dynamics of the EOC chains is not obvious ^[28]. Similar G'' curve is observed (Figure 5-2b). More attention should be paid to the effects of CNT loading on the $\tan\delta$ (Figure 5-2c). The $\tan\delta$ (the ratio of G'' to G') is used to evaluate the composite damping. The $\tan\delta$ is decreased with increasing the CNT loading, exhibiting a corresponding flatter curve.

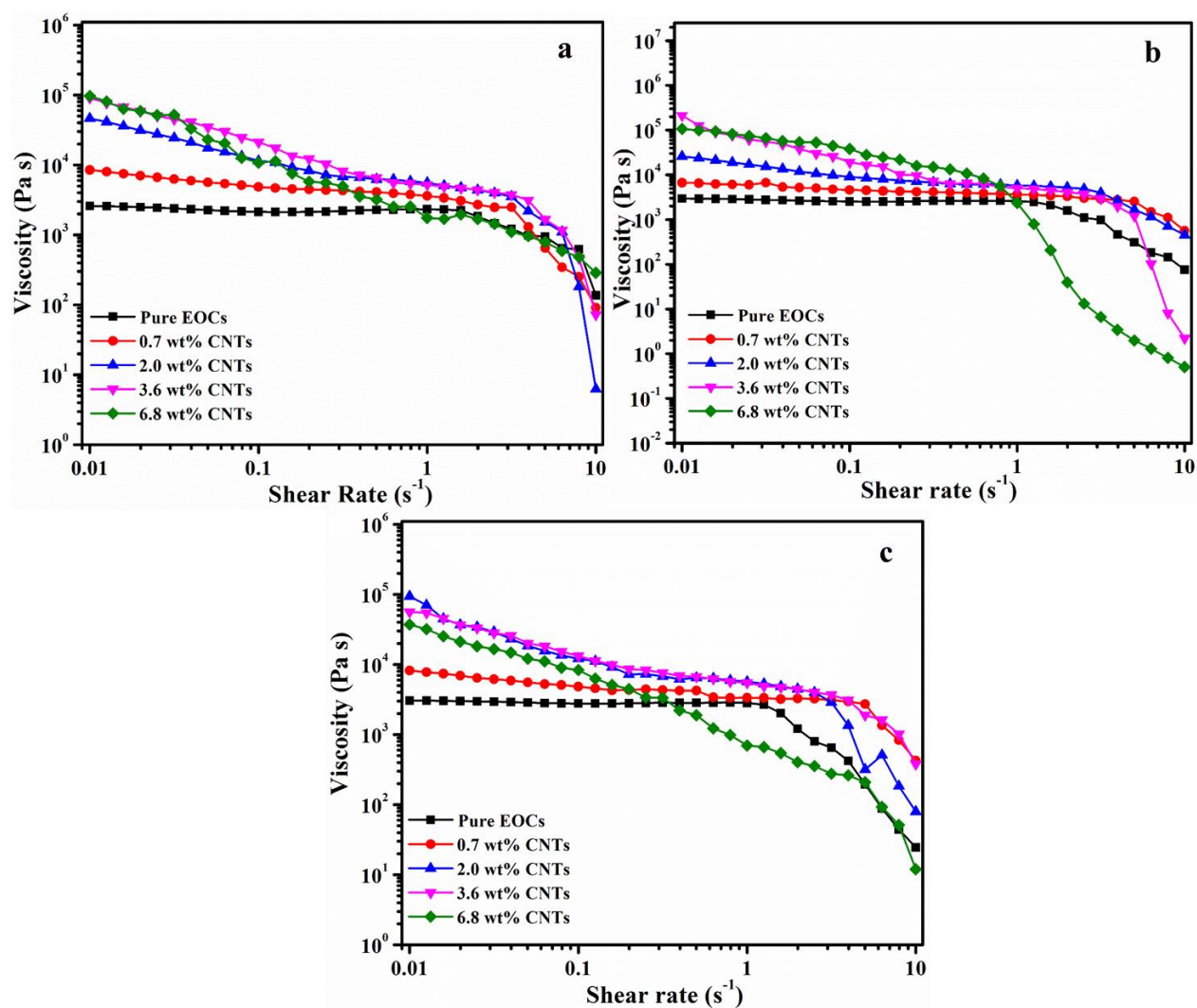


Figure 5-1. Shear rate dependent viscosity of EOCs and EOCs/CNTs nanocomposites melts (measured at 170 °C) with different CNTs loadings made at (a) 100, (b) 120 and (c) 140 °C.

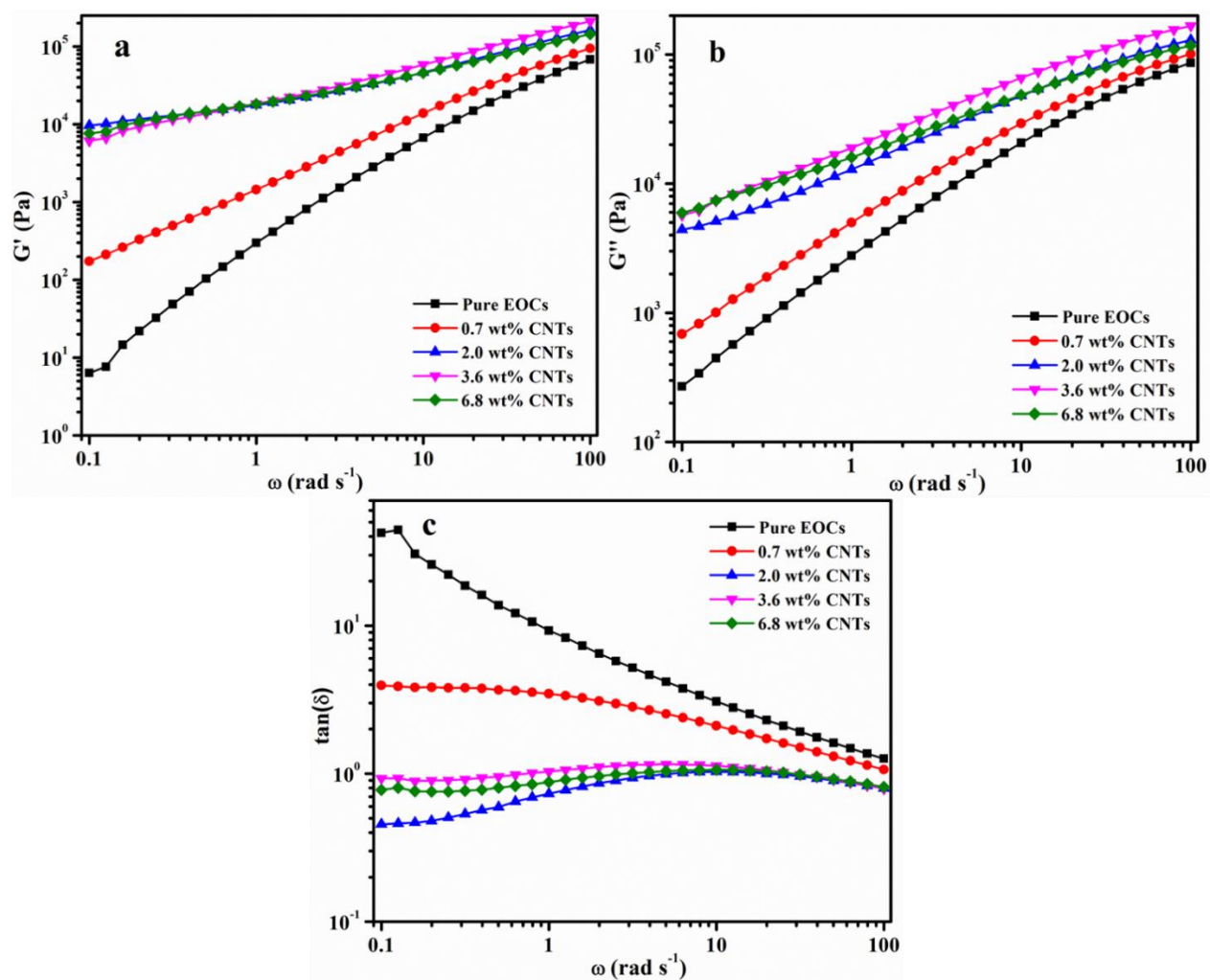


Figure 5-2. Angular frequency (ω) dependent (a) Storage modulus (G'), (b) loss modulus (G''), and (c) loss factor ($\tan\delta$) of neat EOCs and EOCs/CNTs nanocomposites melts (measured at 170 °C) with different CNTs loadings processed at 140 °C.

It is the discordance between strain and stress that causes the mechanical loss in the polymer when it is subjected to an applied frequency dependent external force ^[59]. Meanwhile, the observed higher $\tan\delta$ of neat EOCs than that of the nanocomposites is due to the full relaxation of polymer chains. The relaxation of the polymer chains and the relative motion are hardly restrained by the existing CNTs. Therefore, the friction heat from the internal chains is generated less after applying the same frequency than that of neat EOCs. In addition, the PNCs with higher CNT loadings (≥ 2.0 wt%) have lower $\tan\delta$ values, indicating that a strong CNT-polymer interaction causes less friction heat loss in PNCs than that of pure EOCs ^[60]. A broad peak is observed in the $\tan\delta$ curve and the peak position is shifted to a higher frequency. Both are due to the dissipation of energy and the relaxation of EOC chains.

5.3.2 Crystallinity

Figure 5-3 shows the XRD patterns of pure EOCs and their PNCs. Both mainly exhibit a strong reflection peak followed by a weaker peak, ascribing to the typical orthorhombic unit structure of the (110) and (200) reflection planes ^[61, 62]. It is worth noting that the peak minimum positions of the (110) and (200) are detected at 20.8° and 23.1° for pure EOCs processed at 140 °C, which shift to lower angles compared with that of EOCs processed at 100 °C. It can also be observed from the case of 2.0 wt% nanotube PNCs pressed at 100 and 140 °C. The CNTs affect the crystallite of EOCs. For the crystalline materials, Bragg formula is used to calculate the lattice d -spacing, Equation (1) ^[63],

$$n\lambda = 2d \cdot \sin \theta \quad (1)$$

where n is chosen as 1, λ is the X-ray wavelength ($\lambda = 1.5406$ Å), and θ is the diffraction angle. When θ becomes smaller, the d -spacing will become larger, implying that the increased processing temperature results in an increased effect of the side chains on the crystal phase. But the peak

positions of nanocomposites with 2.0 wt% pressed at 140 °C are shifted to higher angles than those of pure EOCs processed at the same temperature. It appears that the CNTs can prohibit the release of copolymer side-chains in the matrix. Moreover, with a higher processing temperature and the introduction of CNTs, the PNCs with 2.0 wt% CNT loading processed at 140 °C have the highest intensity of these two peaks, arising from the crystalline phase and the large decrease of the half-width of amorphous halo [62].

The Scherrer Equation was used to calculate the average crystallite size, Equation (2) [64],

$$L = \frac{k\lambda}{\beta \cos \theta} \quad (2)$$

where L is the average crystallite size, k is the shape factor, β is the full width at half maximum, and θ is the angle at maximum intensity. The k value depends on the Miller index of reflection plane, the shape of crystal (normally 0.89 if the shape is unknown) and other factors. Here, the $2\theta = 21.2^\circ$ peak of the 2.0 wt% CNTs PNCs is used to calculate and it is about 24.05 nm.

5.3.3 Thermal Stability and Thermal Behavior

Figure 5-4 shows the thermal stability of neat EOCs and composites. For all the samples, there is a sharp weight loss observed in the temperature range from 380 to 510 °C, consistent with the observation in Ketloy's study [65]. Compared with that of pure EOCs, the temperatures of the onset degradation (T_{on}) and 10% mass loss ($T_{10\%}$) are observed to slightly increase with increasing the CNT loading, except for the nanocomposites with 6.8 wt% CNTs, Table 1, showing the stabilization of EOCs by the introduced CNTs. However, when the CNT loading reaches 6.8 wt%, the T_{on} and $T_{10\%}$ decrease arising from high thermal conductivity of CNTs that can transfer heat to

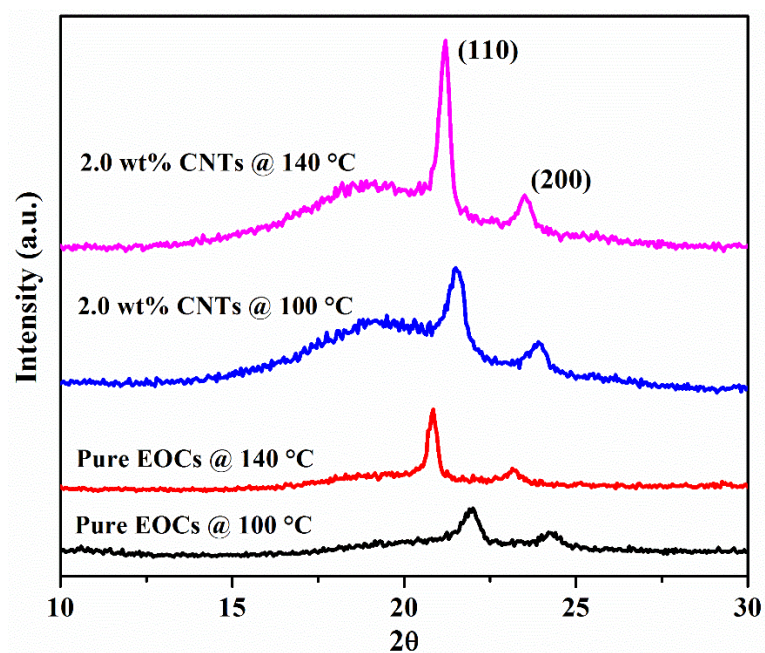


Figure 5-3. XRD curves of EOCs processed at 100 and 140 °C, and the 2.0 wt% CNT nanocomposites made at 100 and 140 °C.

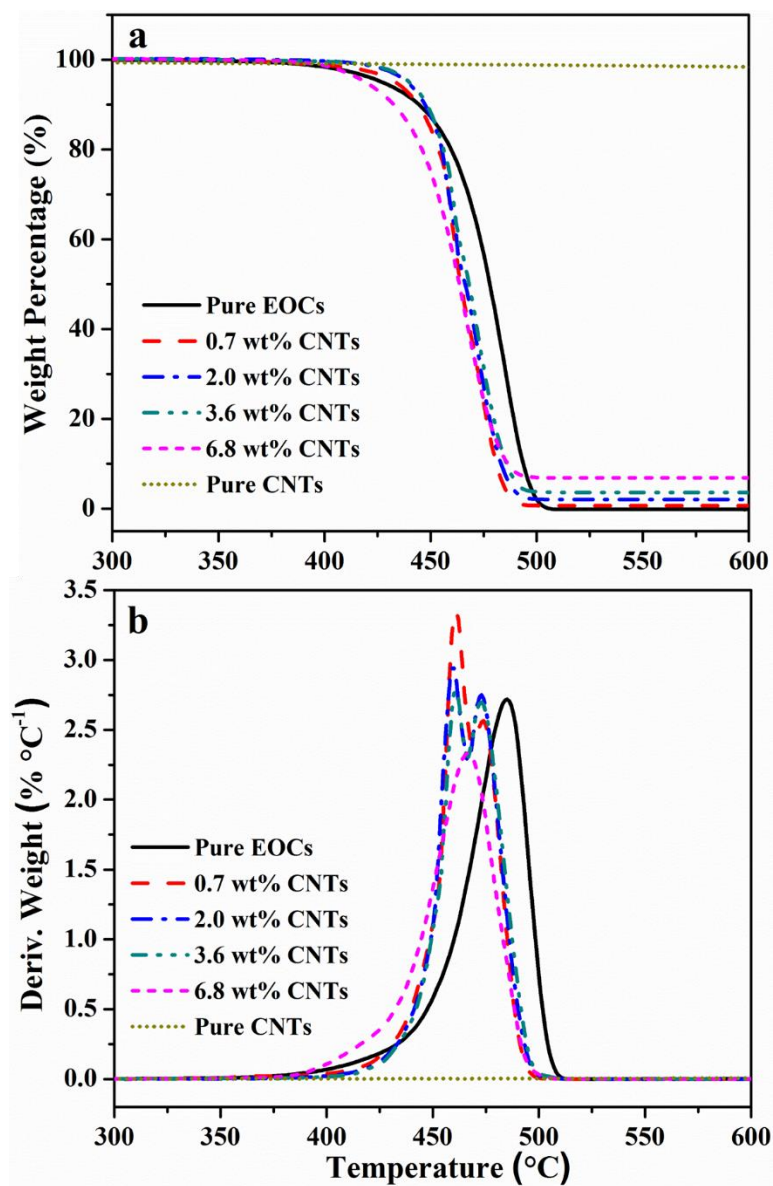


Figure 5-4. a) TGA and b) DTG curve of copolymer and nanocomposites with a nanotube content of 0.7, 2.0, 3.6 and 6.8 wt%, and pure CNTs.

Table 5-1. TGA data of pure copolymer and PNCs.

CNT loading (wt%)	Neat copolymer	0.7 wt%	2.0 wt%	3.6 wt%	6.8 wt%
T_{on} [°C]	405	415	427	429	405
$T_{10\%}$ [°C]	444	444	447	448	432

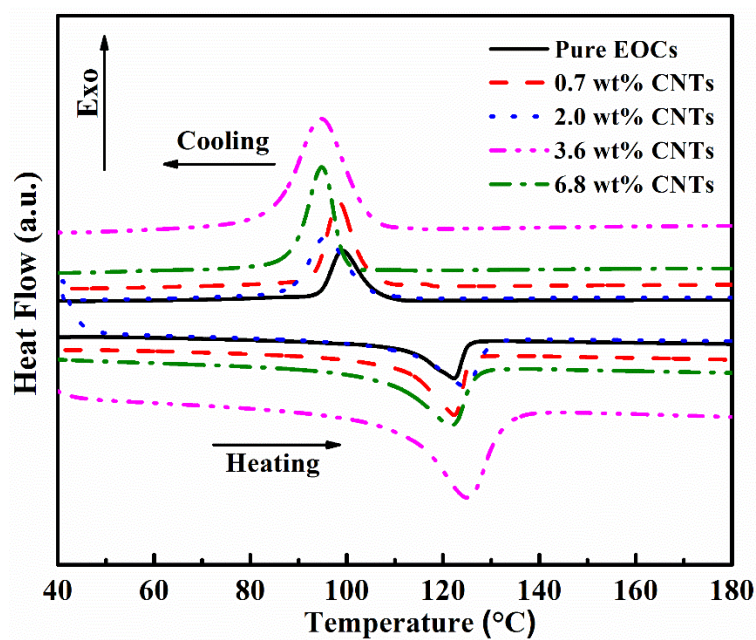


Figure 5-5. DSC curves of copolymer and nanocomposites with a CNTs content of 0.7, 2.0, 3.6 and 6.8 wt%.

Table 5-2. Major parameters from DSC for pure copolymer and its nanocomposites.

CNTs loading (wt%)	T_c (°C)	ΔH_c (J g ⁻¹)	T_m (°C)	ΔH_m (J g ⁻¹)	F_c (%)
Pure copolymer	99.06	43.33	122.04	48.19	16.71
0.7 wt% CNTs	98.35	36.04	122.04	40.06	13.99
2.0 wt% CNTs	95.59	35.93	124.59	39.11	13.84
3.6 wt% CNTs	94.89	35.76	124.98	35.85	12.89
6.8 wt% CNTs	94.86	34.72	123.05	30.02	11.17

the inner part of polymer more quickly. With a careful study of the DTG curves, two peaks in the range from 425 to 500 °C for the PNCs are observed after introducing CNTs, Figure 5-4b, which are due to the strong interfacial interaction between the particle and polymer ^[66]. However, the interfacial interaction is destroyed more quickly in the nanocomposites with increasing the CNT content; therefore, the 6.7 wt% CNT PNCs show one peak. Although lots of nanomaterials such as nanoclays ^[67] and silica nanoparticles ^[68] were used to enhance the thermal stability, only a small increase (typically less than 50 °C) was achieved. This thermal stability of the PNCs in N₂ synthesized by the surface coating approach may supply some guidance to the rational design of thermally stable composites.

The comonomer was introduced as short side chain branches and influenced the microstructure, crystallization, and final shapes of the final copolymers. Their crystallization and melting behaviors were complicated as revealed by several melting endotherms in the DSC results. Figure 5-5 shows the DSC curves of pure EOCs and composites. The exact crystalline peak temperature, T_c ; enthalpy of the crystallization, ΔH_c ; melting peak temperature, T_m ; enthalpy of the fusion, ΔH_m ; and crystalline fraction, F_c , are summarized in Table 2. The ΔH_c and ΔH_m fusion are obtained by directly integrating from the DSC graphs. The first cooling and second heating processes are carried out to study the crystalline behavior and the thermal history effect on the performances of the composites. The pristine EOCs exhibited a T_c of 99.06 °C and a T_m of 122.04 °C. The introduction of α -olefins to the polyethylene chain led to a decreased regularity in the chain structure and resulted in a lower crystallinity, density, and crystallizing and melting points ^[69-71]. Therefore, such copolymers have properties that differ from regular polyethylene. Moreover, for the first cooling process, an increased CNT content is observed to result in a shift of T_c to lower temperatures, since the nanofillers restrained the movement of polymer chains.

However, the T_c of the HDPE/Fe@FeO core-shell system ^[72] is similar to that of neat HDPE, revealing that the introduced nanoparticles did not change the original crystal structure of the matrix. For the second heating process, the T_m of PNCs is observed to be almost the same as that of pure EOCs, indicating that introduced CNTs by the surface coating method did not change the original crystal structure of the hosting polymer. However, the ΔH_m of pure EOCs was decreased from 48.19 to 40.06 J/g when 0.7 wt% CNTs were introduced in EOCs, and decreased to 30.02 J/g further in the composites with 6.8 wt%. The F_c of pure EOCs and nanocomposites can be calculated from Equation (3) ^[73],

$$F_c = \frac{\Delta H_m}{\Delta H_m^0 \times (1-x)} \quad (3)$$

where ΔH_m is the enthalpy of the samples (J/g), and ΔH_m^0 is the enthalpy for a theoretical orthorhombic polyethylene 288.4 (J/g) ^[74] and x is the CNT loading. From the results summarized in Table 2, the F_c is observed to be decreased slightly (2-3%) after the CNTs were introduced into the hosting EOCs. The lower F_c of these PNCs is attributed to the CNTs that destroy the continuous EOC chains. As a result, more grain boundaries and defects were introduced in the EOCs and suppressed the crystallinity.

5.3.4 Thermal Conductivity (λ)

The λ indicates the ability of a material for heat transfer ^[75]. Thermally conductive polymer nanocomposites provide alternatives to replace metal parts in various applications that require high heat dissipation; and low thermal expansion, such as generators, heat exchangers and power electronics, etc. ^[76-78] At present, the most efficient way to improve the λ of polymers is focused

on selectively adding thermally conductive fillers. CNTs seem promising nanofillers, coupling high λ and light weight ^[79, 80]. The normal principle of the FOX heat flow meter instruments is based on 1-D equation for Fourier-Biot law, Equation (4) ^[75],

$$Q = -\lambda (dT/dx) \quad (4)$$

where Q is heat flux (W/m^2) flowing through the sample, λ is the thermal conductivity (W/mK) of the sample, and dT/dx is the temperature gradient (K/m) on the isotherm flat surface in the sample. The thermal resistance (R , $\text{m}^2 \text{ K W}^{-1}$) of the flat samples equals to its thickness (Δx , m) divided by its λ , as shown in Equation (5):

$$R = \Delta x / \lambda \quad (5)$$

Figure 5-6 shows the temperature dependent λ and R curves of neat EOCs and composites. The PNCs with 3.6 wt% CNTs pressed at 120 and 140 °C exhibited higher λ than those of pure EOCs. Meanwhile, the composites with 3.6 wt% CNTs pressed at 140 °C demonstrated higher λ than those of nanocomposites pressed at 120 °C, arising from different CNT network structures formed at different temperatures. Hence, the PNCs with 3.6 wt% CNTs processed at 140 °C showed the lowest R values than those of others, Figure 5-6b. However, the λ values of composites with 0.7 wt% CNTs pressed at 100 and 140 °C are relatively lower than that of the pure polymer matrix. Moisala et al. also reported that the SWNT composites exhibited an initially decreased λ below that of the neat polymer in the composites with a nanotube loading of within 0-0.5 wt% ^[81]. For relative low CNT loading, the main critical issue is that the interfacial R caused by the phonon mismatch at the CNT-polymer interface leads to a high interface R , resulting in serious scattering of the phonons at the interface and a large reduction of thermal transport ^[82]. Therefore, the well formed CNT network can enhance the λ .

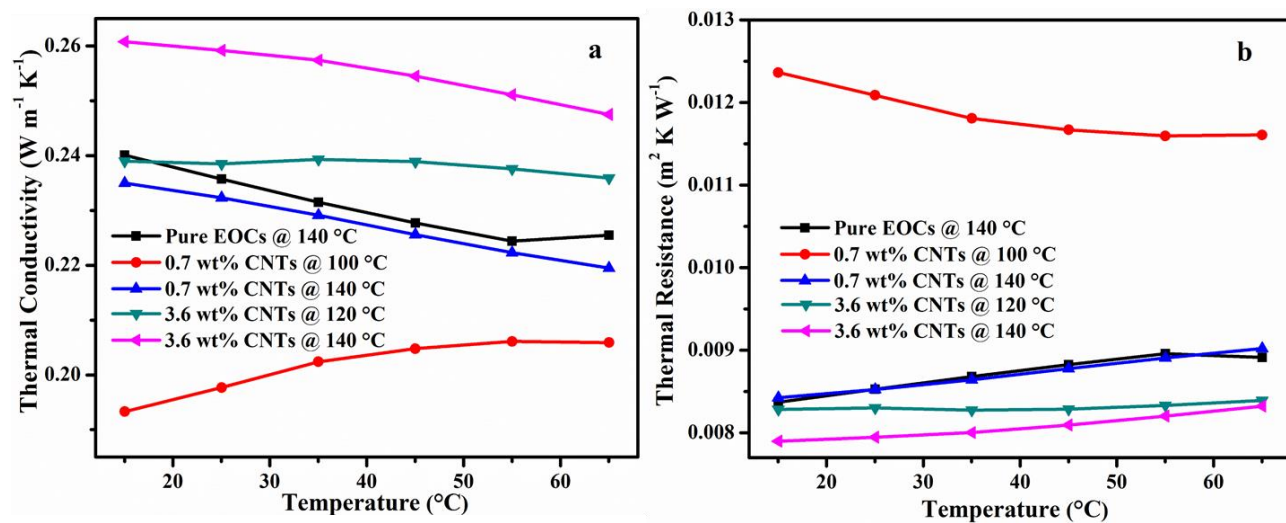


Figure 5-6. a) Thermal conductivity and b) thermal resistance of EOCs processed at 140 $^{\circ}\text{C}$, and 0.7 wt% CNTs nanocomposites made at 100 and 140 $^{\circ}\text{C}$, 3.6 wt% CNTs nanocomposites made at 120 and 140 $^{\circ}\text{C}$.

5.3.5 Electronic Property of EOC/CNT Nanocomposites

The electronic properties are very important for material applications, including thin film transistors^[83], solar cells^[84], and chemical/biochemical sensors^[85]. The optical properties of pure CNTs and their nanocomposites were investigated using the UV-vis spectra. The band gap (E_g) value of a sphere was calculated from a photon-energy ($h\nu$) dependent $\alpha h\nu$ obtained from the diffuse reflectance UV-Vis spectra by using Equation (6) (Tauc's plot^[86]),

$$\alpha h\nu = (h\nu - E_g)^n \quad (6)$$

where α , h and ν are the coefficient of the absorbance, Planck's constant and photon frequency. The Tauc plot was obtained by converting from the diffuse reflectance UV-vis spectrum. The parameter n is a pure number related to the transition type of electrons ($n=0.5$, and $= 2$ for the allowed direct, and indirect transitions, respectively)^[87, 88]. For CNTs, the reported n was ~ 2 ^[89] and the E_g was calculated by extrapolating from the energy axis in the linear part of the curve. The calculated E_g of pure CNTs was ~ 1.50 eV, Figure 5-7a, comparable to the 1.543 eV reported for the transition above the second pair of van Hove singularity and lower than the Fermi level of carbon nanotubes with an index of (9,8)^[90].

The 6.8 wt% PNCs processed at 100 °C show a much lower band gap of 0.86 eV, Figure 5-7c, suitable for using as semiconductors^[91]. This phenomenon can be interpreted from the point of electron quantum states. According to the Pauli exclusion principle, the electrons can be classified into state zero or state one^[92]. The σ takes place arising from the existing electrons in the delocalized states. An orbital must be partly filled with electrons; otherwise, with a full filling, the orbital is inert to block the transport of other electrons. Appropriately partially filled states and the delocalization state, arising from the formed network of CNTs, led to a lower E_g . Moreover,

with the same loading of CNTs (Figure 5-7d&e, c&f), the E_g of the nanocomposites is dependent on the pressing temperature. The E_g variance is possibly due to the hot-press induced strain of the CNTs. The strain effect on the E_g of the CNTs is complex since the CNT strain could play a positive or negative role in the electron transport. The strain can lead to the insulation-conduction transition of SWNTs arising from the varied quantum number ^[93, 94]. However, uniaxial strain in graphene causes the red shift of the 2D and G band, arising from the elongation of the C-C bonds ^[95]. For the EOC/CNT system, the E_g is reduced at higher CNT content (Figure 7b,d&f). The changing trend of E_g corresponds to the σ value in the PNCs; i.e., the nanocomposites with higher σ showed a reduced E_g .

5.3.6 Electrical Conductivity (σ) of EOC/CNT Nanocomposites

Figure 5-8 shows the σ variation of the nanocomposites at different CNT loadings with different processing temperatures. The σ is increased with increasing the CNT content, and the 6.8 wt% CNT nanocomposites pressed at 100 °C show the highest σ of 0.015 S/cm, three orders of magnitude larger than that of the PP nanocomposites even with 5 wt% CNT loading ^[96]. The higher σ was ascribed to the formed conductive CNT network. At 100 °C, the EOC pellets coated with CNTs just start to melt. The pellets would only change the shape without destroying the CNT coating during the hot press, and the CNTs would be pressed together, Scheme 5-1(a). At 120 °C, the pellets were under melting state, and the CNT layer on the surface was easier to be broken and moved to the matrix, Scheme 5-1(b). Therefore, some parts of the CNT network were destroyed. However, at 140 °C, the PNCs were totally molten, and more CNTs were released from the layer and diffused into the polymer matrix. The network still existed, but the density of network was lower than that at 100 °C, Scheme 5-1(c). These can well explain the lower σ

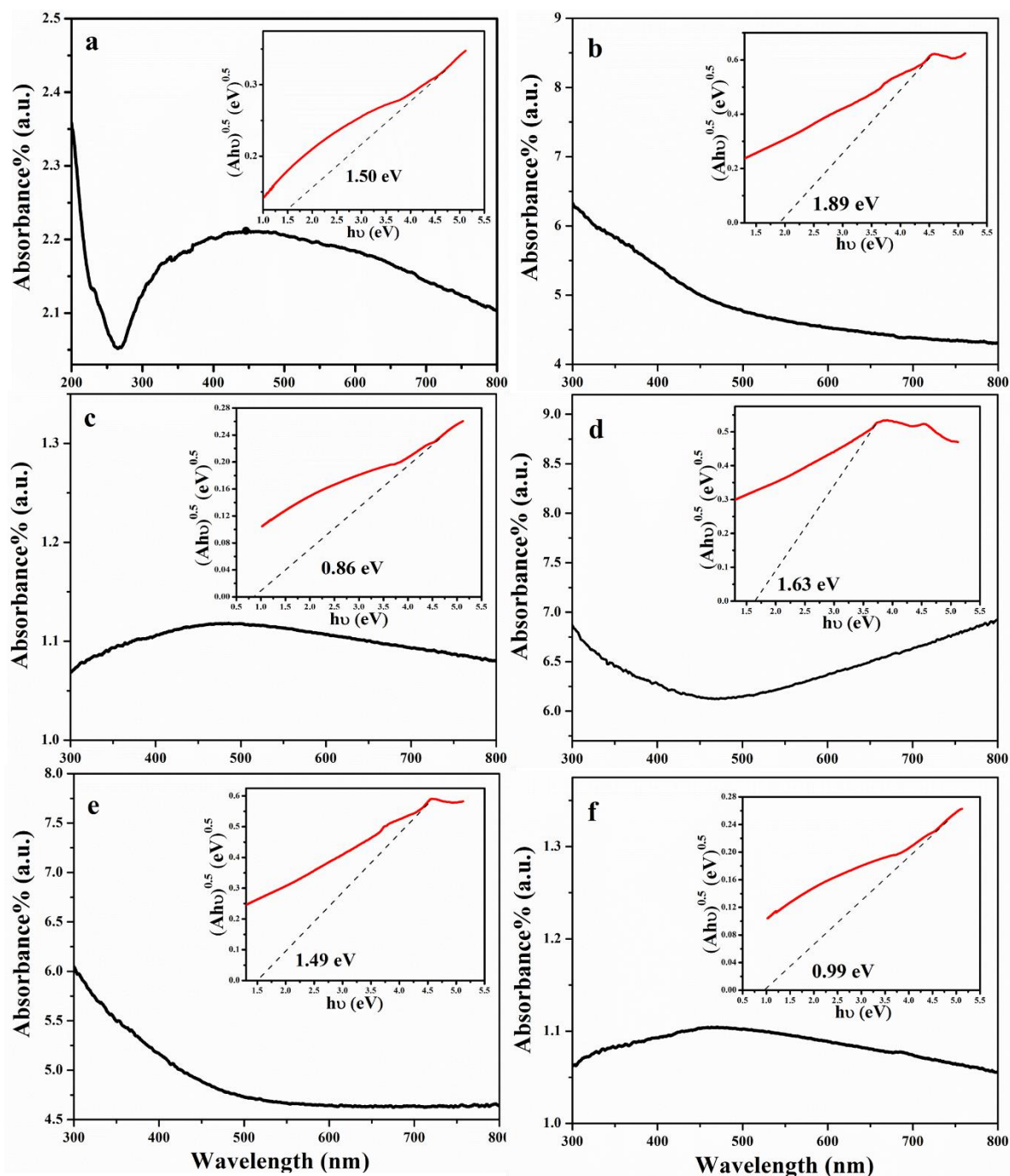


Figure 5-7. UV-vis absorbance spectrum (converted from diffuse reflectance spectrum data) of: a) nanotubes; Nanocomposites made at 120 °C with b) 2.0, d) 3.6 and f) 6.8 wt% CNTs loadings; c) nanocomposites made at 100 °C with 6.8 wt% CNTs loadings; e) nanocomposites made at 140 °C with 3.6 wt% CNTs content. The insets depict the Figure to obtain the bandgap for a direct bandgap transition for a-f, respectively.

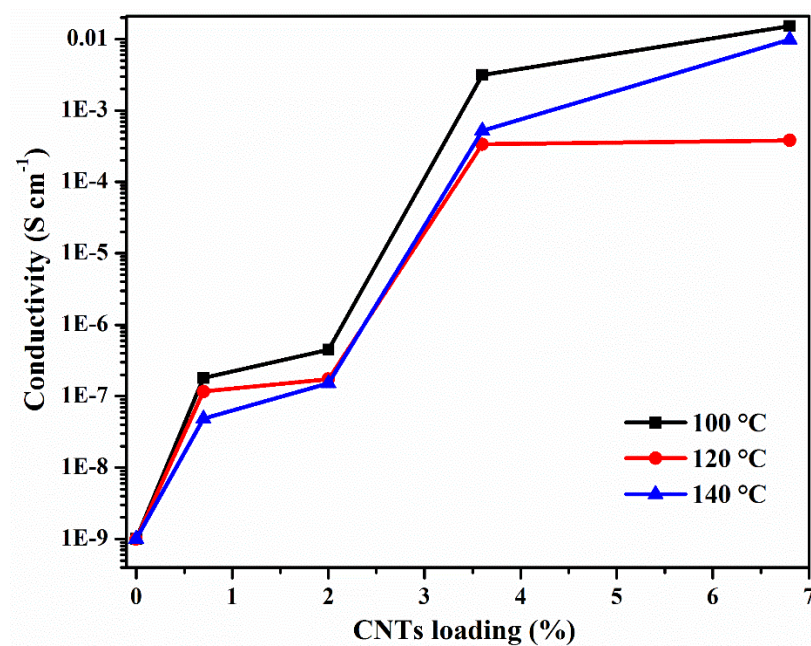
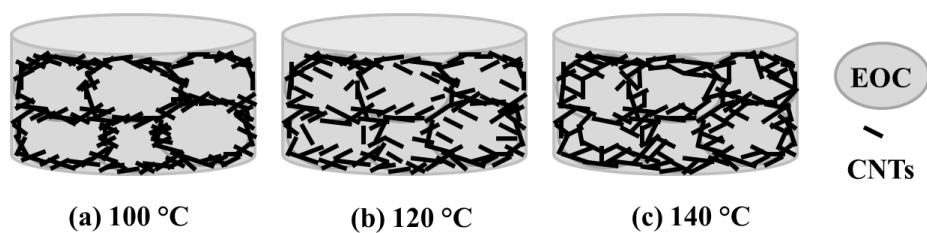


Figure 5-8. CNTs loading dependent electrical conductivity of nanocomposites for the samples made at 100, 120 and 140 °C.



Scheme 5-1. The morphology of nanocomposites at different pressing temperatures (not scaled).

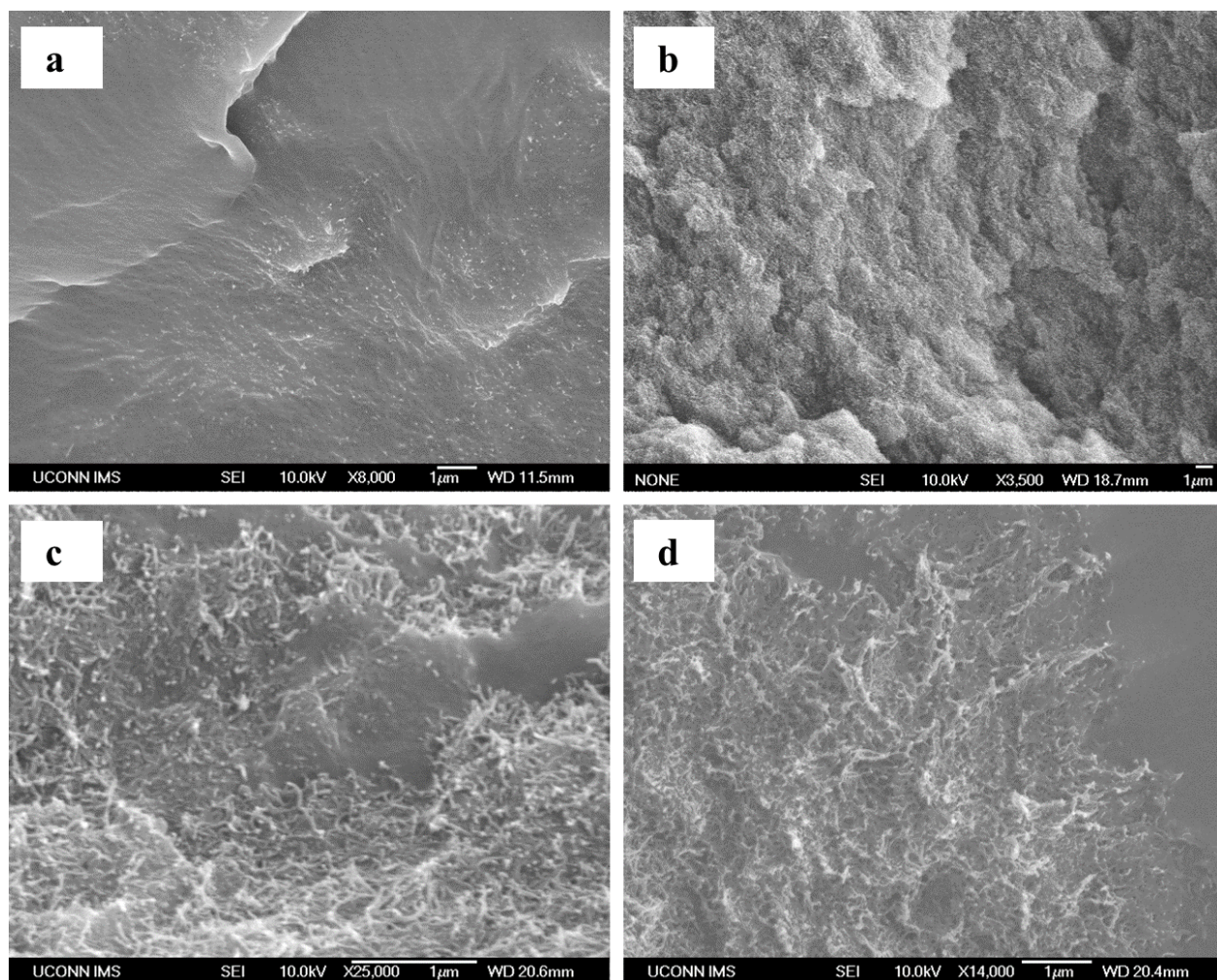


Figure 5-9. SEM graphs of nanocomposites with 2.0 wt% CNTs made at a) 100 °C and nanocomposites with 6.8 wt% CNTs made at b) 100, c) 120 and d) 140 °C.

in the 6.8 wt% CNT PNCs processed at 140 °C than their processed at 100 °C, and higher σ than those processed at 120 °C. This can be verified by a morphological study, Figure 5-9. For the 2.0 wt% CNT nanocomposites prepared at 100 °C, the pellets were observed with surface deformed and coated with CNTs, Figure 5-9a. The network structure is observed with 2.0 wt% CNTs in PNCs pressed at 100 °C, indicating a low percolation concentration for the PNCs ^[97]. The CNTs are observed to agglomerate to form network structures, Figure 5-9(b-c), thereby leading to a sharp increase in σ . However, for the nanocomposites made at 120 °C, the CNT coating was separated by EOCs since the matrix began to melt, Figure 5-9c. The conducting paths arose from the CNTs. At increased temperatures (for example, 120 and 140 °C), since the diffusion of the CNTs to the EOC matrix caused the dispersion of the CNTs, and limited CNTs can form conductive path, Figure 9c-d ^[98]. However, the network density rises since more nanotubes became involved in the formation of conductive network, when the PNCs were prepared at low temperature (100 °C), leading to a higher σ ^[98].

5.3.7 Temperature Dependent Resistivity – Electrical Conductivity Mechanism

Figure 5-10a shows the temperature dependent resistivity for the nanocomposites with 2.6 and 3.0 wt% CNTs made at 120 and 140 °C. For all samples, the resistivity is decreased with increase of the temperature, indicating a semiconducting behavior within the measured 45-220 K region ^[99]. The PNCs obey the following resistivity changing trend: 2.0 wt% CNTs@120 °C > 2.0 wt% CNTs@140 °C > 3.6 wt% CNTs@120 °C > 3.6 wt% CNTs@140 °C. The resistivity is observed to follow the variable range hopping (VRH) theory, which depends on the network structure in the polymer matrix. The electron transport mechanism was exploited by the temperature- σ VRH relationship, Equation (7) ^[100],

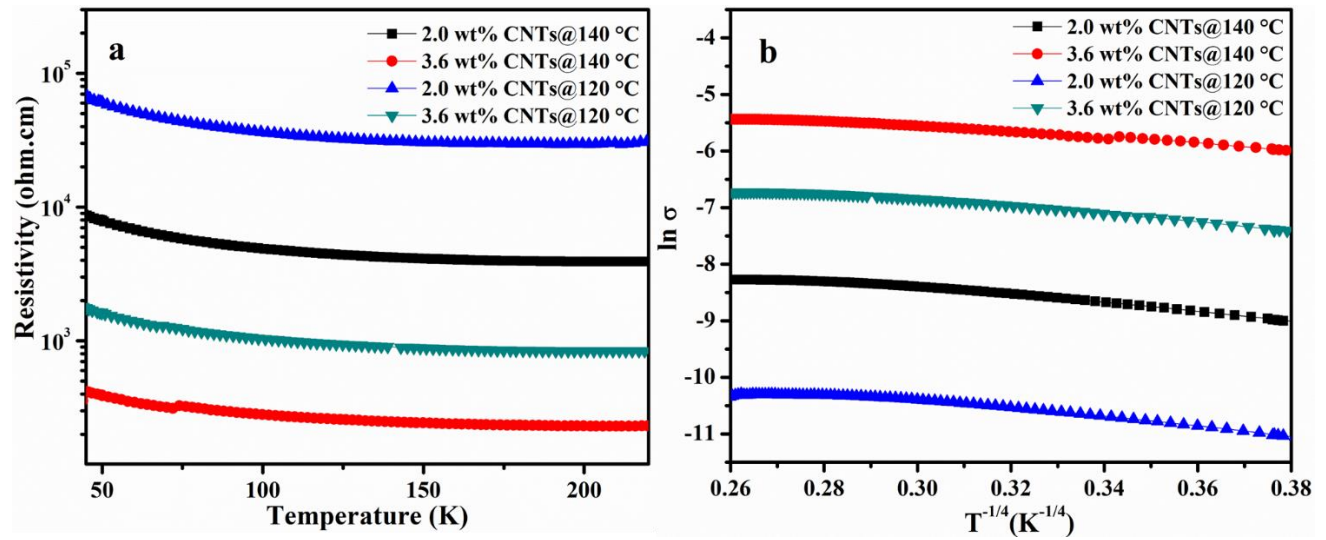


Figure 5-10. a) Temperature dependent resistivity, and b) $\ln(\sigma)$ vs $T^{-1/4}$ curves of CNTs nanocomposites.

Table 5-3. T_0 and σ_0 for the EOC/CNT PNCs.

Samples	T_0 (K)	$\sigma_0 \times 10^4$ (S/cm)
2.0 wt% CNTs@120 °C	2868.05	2.75
2.0 wt% CNTs@140 °C	2138.57	17.36
3.6 wt% CNTs@120 °C	2076.80	80.61
3.6 wt% CNTs@140 °C	1087.84	216.43

$$\sigma = \sigma_0 \exp \left[- \left(\frac{T_0}{T} \right)^{1/(n+1)} \right] \quad (7)$$

where the constant T_0 (K) is the characteristic Mott temperature associated with the electronic wave function localization degree, σ_0 is the conductivity at infinitely low temperature, T is the Kelvin temperature, and n can be 1, 2 or 3, standing for one-, two-, or three- dimensional systems, respectively. Figure 5-10b shows the best linear fits of $\ln(\sigma) \sim T^{-1/(n+1)}$ for PNCs (Figure 5-10a) with $n = 3$ in the 45 ~ 220 K range. This indicates a 3-d electron transport mechanism. This means that the PNC systems with 2.6 and 3.0 wt% nanotubes respectively made at 120 and 140 °C are disordered in the 3-d VRH regime. The T_0 and σ_0 values can be calculated from the intercept and the slope of the plot $\ln(\sigma) \sim T^{-1/(n+1)}$; Table 5-3 shows the summarized results. The T_0 value of the composites obeys the following order: 2.0 wt% CNTs@120 °C > 2.0 wt% CNTs@140 °C > 3.6 wt% CNTs@120 °C > 3.6 wt% CNTs@140 °C, which is consistent with the measured resistivity values. The σ_0 rises with decreasing processing temperature within a certain CNT loading. In general, a larger T_0 indicates a stronger localization of the charge carriers in the system and thus represents a lower $\sigma^{[101]}$. Therefore, these results also prove that, although the nanofillers have free movement in the matrix at higher temperature, the network is still formed with lower density of CNTs.

5.3.8 Magnetoresistance (MR)

Figure 5-11 shows the magnetoresistance (MR) of 2.6 wt% nanotube reinforced nanocomposites made at 120 °C, and 3.0 wt% nanotube PNCs pressed at 140 °C. The MR is calculated using Equation (8) ^[102],

$$\text{MR}\% = \frac{R(H, T) - R(0, T)}{R(0)} \times 100 \quad (8)$$

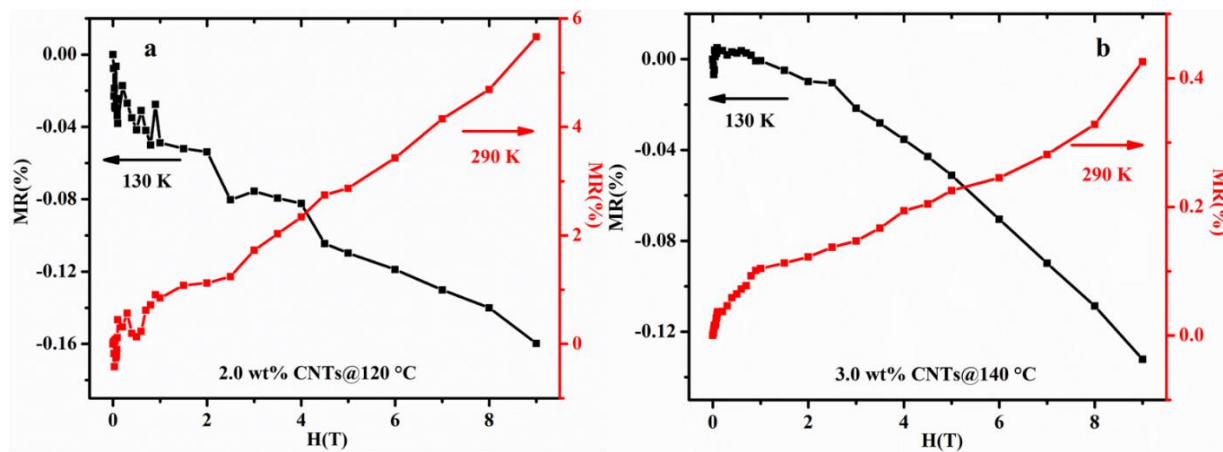


Figure 5-11. Magnetoresistance of nanocomposites with a CNTs loading of a) 2.6 wt% processed at 120 °C, and b) 3.0 wt% processed at 140 °C. The MR was measured at 130 and 290 K.

where $R(0, T)$ and $R(H, T)$ are the resistance with zero field and under a magnetic field H . The MR results show different field dependent behavior and can be classified to two groups. The first is the relatively large positive MR measured at 290 K (red curves), the other is negative MR from PNCs measured at 130 K (black curves). The positive MR is due to the shrinkage in the overlap of the wave function of the electrons after applying a field and thus a decreased average hopping length ^[103]. The wave function shrinkage model is normally used to depict the positive magnetoresistance and the $R(H,T)/R(0,T)$ ratio can be expressed as Equation (9) ^[104],

$$R(H, T) / R(0, T) = \exp\{\xi_c(0)[\xi_c(H) / \xi_c(0) - 1]\} \quad (9)$$

where $\xi_c(0) = (T_0 / T)^{1/4}$ for the 3 dimensional Mott VRH transport; $\xi_c(H) / \xi_c(0)$ is H/P_C dependent normalized hopping probability parameter for the Mott VRH charge transport mechanism; H is the field (Tesla, $1 \text{ T} = 10^4 \text{ Oe}$, $T = \text{kg C}^{-1} \text{ s}^{-1}$); The fitting parameter P_C , the normalizing field to be extracted from the MR ratios, is calculated by Equation (10) for the Mott VRH transposition ^[104, 105],

$$P_C = 6\hbar / [ea_0^2 (T_0 / T)^{1/4}] \quad (10)$$

where e is electron charge ($1.6021765 \times 10^{-19}$), $\hbar$ is the reduced Planck's constant, and $\hbar = h/2\pi$, h is the Planck's constant. In the low field limit, especially considering the non-magnetic materials, Equation 10 is simplified to Equation (11),

$$R(H, T) / R(0, T) \approx 1 + t_2 \frac{H^2}{P_C^2} \left(\frac{T_0}{T} \right)^{1/4} \quad (11)$$

and MR is defined as Equation (12),

$$\text{MR} = \frac{R(H, T) - R(0, T)}{R(0, T)} \approx t_2 \frac{H^2}{P_C^2} \left(\frac{T_0}{T} \right)^{1/4} = t_2 \frac{e^2 a_0^4}{36\hbar^2} \left(\frac{T_0}{T} \right)^{3/4} H^2 \quad (12)$$

where the numerical constant $t_2 = 5/2016$.

According to Equation (12), the localization length a_0 can be calculated by Equation 12 from T_0 , MR values, and H :

$$a_0^4 = \frac{36\hbar^2 MR}{t_2 e^2} \left(\frac{T_0}{T}\right)^{-3/4} H^{-2} \quad (13)$$

The calculated a_0 of EOCs/CNTs PNCs is listed in Table 5-4. The a_0 is observed to be decreased with the increase of the H ; and the higher MR accompanies with a smaller a_0 . The R_{hop} (average hopping length) can be calculated from Equation (14) by T_0 , T and a_0 ^[106],

$$R_{\text{hop}} = (3/8)(T_0/T)^{1/4} a_0 \quad (14)$$

Table 5-4 summarizes the calculated R_{hop} , which is H dependent. In a hopping system, the magnetoresistance comes from the charge hopping conduction due to the wave function contraction of the charge carriers and the following decreased R_{hop} . ^[107] Thus, the R_{hop} is decreased with the increase of the H and the MR rises with the increase of the H , indicating that the MR value is related to the R_{hop} .

The negative magnetoresistance effect of these nanocomposites can be interpreted by the orbital magnetoconductivity theory ^[47]. The interferences among these hopping paths were considered in this theory. The conducting paths will include a series of scattering for the tunneling electrons by the impurities that are located within the cigar shape domain with a length of r_h and a width of $(r_h a_0)^{1/2}$ ^[108]. The negative MR decreases with the increase of the H . At 130 K, the MR of nanocomposites with 2.0 wt% CNTs prepared at 120 °C and with 3.0 wt% CNTs made at 140 °C are -0.16 % and -0.12 %, respectively. The negative MR is also obtained in the bulk samples of SWCNTs ^[109]. The lower measured temperature causes a reduced resistance within the CNT network, causing a negative magnetoresistance. This MR switching phenomenon with different temperature

Table 5-4. The a_0 for EOC/CNT PNCs at different magnetic fields H .

Samples	Parameters	Magnetic Field (H, T)		
		1	4	9
2.0 wt% CNTs@120 °C	a_0 (nm)	55.62	35.83	29.79
	R_{hop} (nm)	36.99	23.83	19.81
3.6 wt% CNTs@140 °C	a_0 (nm)	39.49	23.06	18.71
	R_{hop} (nm)	20.61	12.03	9.76

demonstrated in these nanocomposites provides a great opportunity to obtain MR with desired values.

5.4. Conclusions

Ethylene/1-octene copolymer (EOC) nanocomposites with different loading levels of CNTs were prepared by sticking the CNTs on the gelated EOC pellet surface. A strong CNT-polymer interaction led to less friction heat loss in the PNCs than pure EOCs. SEM observations showed that the CNTs were pressed tighter and a network structure was formed and gave a higher electrical conductivity. Both XRD and DSC results revealed a constant crystalline structure of EOCs during the synthesis of EOC PNCs. The CNTs acted as a heat transfer medium in the matrix, depending on the CNT loading level. All pure EOCs and the PNCs revealed both Newtonian and shear thinning (power law) behaviors in the melt states. The observed rheological plateau in the low oscillation frequency region was due to the formed network of CNTs in the hosting EOC matrix. Finally, the varying trend of E_g in these nanocomposites corresponded to the σ value of PNCs; the nanocomposites with higher σ showed a lower E_g . Variable range hopping revealed a 3-d electron transport in the PNCs with 2.6 and 3.0 wt% nanotubes, respectively, made at 120 and 140 °C. Both positive and negative MR can be obtained by fabricating PNCs at different temperatures, offering a promising approach to achieve desired MR devices.

5.5. References

- [1] X. Zhang, X. Yan, J. Guo, Z. Liu, D. Jiang, Q. He, H. Wei, H. Gu, H. A. Colorado, X. Zhang, *J. Mater. Chem. C* **2015**, 3, 162.
- [2] Q. He, T. Yuan, X. Zhang, X. Yan, J. Guo, D. Ding, M. A. Khan, D. P. Young, A. Khasanov, Z. Luo, *J. Phys. Chem. C* **2014**, 118, 24784.
- [3] H. Gu, J. Guo, X. Yan, H. Wei, X. Zhang, J. Liu, Y. Huang, S. Wei, Z. Guo, *Polymer* **2014**, 55, 4405.
- [4] L. Sun, G. L. Warren, H.-J. Sue, *Carbon* **2010**, 48, 2364.
- [5] P. Ajayan, O. Stephan, C. Colliex, D. Trauth, *Science* **1994**, 265, 1212.
- [6] A. S. Aricò, P. Bruce, B. Scrosati, J.-M. Tarascon, W. Van Schalkwijk, *Nat. Mater.* **2005**, 4, 366.
- [7] A. Rudge, J. Davey, I. Raistrick, S. Gottesfeld, J. P. Ferraris, *J. Power Sources* **1994**, 47, 89.
- [8] J. Zhu, H. Gu, Z. Luo, N. Haldolaarachige, D. P. Young, S. Wei, Z. Guo, *Langmuir* **2012**, 28, 10246.
- [9] H. Gu, J. Guo, H. Wei, Y. Huang, C. Zhao, Y. Li, Q. Wu, N. Haldolaarachchige, D. P. Young, S. Wei, *PCCP* **2013**, 15, 10866.
- [10] H. Gu, J. Guo, X. Zhang, Q. He, Y. Huang, H. A. Colorado, N. Haldolaarachchige, H. Xin, D. P. Young, S. Wei, *J. Phys. Chem. C* **2013**, 117, 6426.
- [11] L. J. Lee, C. Zeng, X. Cao, X. Han, J. Shen, G. Xu, *Compos. Sci. Technol.* **2005**, 65, 2344.
- [12] R. Rahimi, M. Ochoa, W. Yu, B. Ziaie, *ACS Appl. Mater. Interfaces* **2015**, 7, 4463.
- [13] M. Amjadi, A. Pichitpajongkit, S. Lee, S. Ryu, I. Park, *ACS nano* **2014**, 8, 5154.
- [14] T. Kashiwagi, E. Grulke, J. Hilding, K. Groth, R. Harris, K. Butler, J. Shields, S. Kharchenko, J. Douglas, *Polymer* **2004**, 45, 4227.
- [15] X. Yan, Q. He, X. Zhang, H. Gu, H. Chen, Q. Wang, L. Sun, S. Wei, Z. Guo, *Macromol. Mater. Eng.* **2014**, 299, 485.
- [16] V. Hadjiev, G. Warren, L. Sun, D. Davis, D. Lagoudas, H.-J. Sue, *Carbon* **2010**, 48, 1750.
- [17] J. Zhu, S. Wei, N. Haldolaarachchige, D. P. Young, Z. Guo, *J. Phys. Chem. C* **2011**, 115, 15304.
- [18] Z. Guo, S.-E. Lee, H. Kim, S. Park, H. Hahn, A. Karki, D. Young, *Acta Mater.* **2009**, 57, 267.
- [19] Z. Guo, S. Park, H. T. Hahn, S. Wei, M. Moldovan, A. B. Karki, D. P. Young, *J. Appl. Phys.* **2007**, 101, 09M511.
- [20] J. Njuguna, K. Pielichowski, *Adv. Eng. Mater.* **2003**, 5, 769.
- [21] C. Cooper, R. Young, M. Halsall, *Composites Part A* **2001**, 32, 401.
- [22] L. Sun, G. Warren, D. Davis, H.-J. Sue, *J. Mater. Sci.* **2011**, 46, 207.
- [23] G. Gao, T. Cagin, W. A. Goddard III, *Nanotechnology* **1998**, 9, 184.
- [24] X. Wang, Q. Li, J. Xie, Z. Jin, J. Wang, Y. Li, K. Jiang, S. Fan, *Nano Lett.* **2009**, 9, 3137.
- [25] L. Sun, G. Warren, J. O'reilly, W. Everett, S. Lee, D. Davis, D. Lagoudas, H.-J. Sue, *Carbon* **2008**, 46, 320.
- [26] T. Uchida, S. Kumar, *J. Appl. Polym. Sci.* **2005**, 98, 985.
- [27] S. Iijima, *Nature* **1991**, 354, 56.
- [28] F. Du, R. C. Scogna, W. Zhou, S. Brand, J. E. Fischer, K. I. Winey, *Macromolecules* **2004**, 37, 9048.
- [29] X. Zhang, X. Yan, Q. He, H. Wei, J. Long, J. Guo, H. Gu, J. Yu, J. Liu, D. Ding, *ACS Appl. Mater. Interfaces* **2015**, 7, 6125.

- [30] T. Kashiwagi, E. Grulke, J. Hilding, R. Harris, W. Awad, J. Douglas, *Macromol. Rapid Commun.* **2002**, 23, 761.
- [31] L. Hu, D. Hecht, G. Grüner, *Nano Lett.* **2004**, 4, 2513.
- [32] A. A. Koval'chuk, A. N. Shchegolikhin, V. G. Shevchenko, P. M. Nedorezova, A. N. Klyamkina, A. M. Aladyshev, *Macromolecules* **2008**, 41, 3149.
- [33] J. Sandler, J. Kirk, I. Kinloch, M. Shaffer, A. Windle, *Polymer* **2003**, 44, 5893.
- [34] X. Chen, H. Wang, H. Yi, X. Wang, X. Yan, Z. Guo, *J. Phys. Chem. C* **2014**, 118, 8262.
- [35] S. Barrau, P. Demont, E. Perez, A. Peigney, C. Laurent, C. Lacabanne, *Macromolecules* **2003**, 36, 9678.
- [36] Y. J. Kim, T. S. Shin, H. D. Choi, J. H. Kwon, Y.-C. Chung, H. G. Yoon, *Carbon* **2005**, 43, 23.
- [37] S. Bose, R. A. Khare, P. Moldenaers, *Polymer* **2010**, 51, 975.
- [38] F. H. Gojny, M. H. Wichmann, B. Fiedler, I. A. Kinloch, W. Bauhofer, A. H. Windle, K. Schulte, *Polymer* **2006**, 47, 2036.
- [39] I. W. Hamley, *"The physics of block copolymers"*, Oxford University Press New York, 1998.
- [40] J. Zhu, S. Wei, J. Ryu, Z. Guo, *J. Phys. Chem. C* **2011**, 115, 13215.
- [41] S. Mecking, L. K. Johnson, L. Wang, M. Brookhart, *J. Am. Chem. Soc.* **1998**, 120, 888.
- [42] M. Lopez-Manchado, M. Arroyo, *Polymer* **2001**, 42, 6557.
- [43] K. Premphet, P. Horanont, *Polymer* **2000**, 41, 9283.
- [44] C. Li, Y. Zhang, Y. Zhang, C. Zhang, *Eur. Polym. J.* **2003**, 39, 305.
- [45] M. J. O. Guimarães, F. Coutinho, M. C. Rocha, M. Farah, R. E. Bretas, *J. Appl. Polym. Sci.* **2002**, 86, 2240.
- [46] Z. Guo, S. Park, H. T. Hahn, S. Wei, M. Moldovan, A. B. Karki, D. P. Young, *Appl. Phys. Lett.* **2007**, 90, 053111.
- [47] J. Guo, H. Gu, H. Wei, Q. Zhang, N. Haldolaarachchige, Y. Li, D. P. Young, S. Wei, Z. Guo, *J. Phys. Chem. C* **2013**, 117, 10191.
- [48] J. Zhu, M. Chen, H. Qu, H. Wei, J. Guo, Z. Luo, N. Haldolaarachchige, D. P. Young, S. Wei, Z. Guo, *J. Mater. Chem. C* **2014**, 2, 715.
- [49] H. Gu, X. Zhang, H. Wei, Y. Huang, S. Wei, Z. Guo, *Chem. Soc. Rev.* **2013**, 42, 5907.
- [50] H. Gu, J. Guo, H. Wei, S. Guo, J. Liu, Y. Huang, M. A. Khan, X. Wang, D. P. Young, S. Wei, *Adv. Mater.* **2015**, 27, 6277.
- [51] M. Wang, W. Wang, T. Liu, W.-D. Zhang, *Composites Science and Technology* **2008**, 68, 2498.
- [52] E. E. Rosenbaum, S. G. Hatzikiriakos, C. W. Stewart, *Rheol. Acta* **1998**, 37, 279.
- [53] A. Tuteja, P. M. Duxbury, M. E. Mackay, *Macromolecules* **2007**, 40, 9427.
- [54] S. Jain, J. G. P. Goossens, G. W. M. Peters, M. van Duin, P. J. Lemstra, *Soft Matter* **2008**, 4, 1848.
- [55] B. Wang, L. Hao, W. Wang, G. Hu, *J. Polym. Res.* **2010**, 17, 821.
- [56] C. A. Mitchell, J. L. Bahr, S. Arepalli, J. M. Tour, R. Krishnamoorti, *Macromolecules* **2002**, 35, 8825.
- [57] P. Pötschke, M. Abdel-Goad, I. Alig, S. Dudkin, D. Lellinger, *Polymer* **2004**, 45, 8863.
- [58] J. Zhu, S. Wei, A. Yadav, Z. Guo, *Polymer* **2010**, 51, 2643.
- [59] W. Xue-Bang, X. Qiao-Ling, S. Shu-Ying, S. Jia-Peng, L. Chang-Song, Z. Zhen-Gang, *Chinese Physics Letters* **2008**, 25, 1388.

- [60] Y. Gao, Q. Wang, J. Wang, L. Huang, X. Yan, X. Zhang, Q. He, Z. Xing, Z. Guo, *ACS Appl. Mater. Interfaces* **2014**, 6, 5094.
- [61] M. a. L. Cerrada, R. Benavente, E. Pérez, J. Moniz-Santos, M. R. Ribeiro, *Polymer* **2001**, 42, 7197.
- [62] R. Androsch, *Polymer* **1999**, 40, 2805.
- [63] B. C. Giessen, G. E. Gordon, *Science* **1968**, 159, 973.
- [64] J. Deng, X. Ding, W. Zhang, Y. Peng, J. Wang, X. Long, P. Li, A. S. C. Chan, *Polymer* **2002**, 43, 2179.
- [65] C. Ketloy, B. Jongsomjit, P. Praserttham, *Appl. Catal., A* **2007**, 327, 270.
- [66] X. Yan, M. Li, J. Long, X. Zhang, H. Wei, Q. He, D. Rutman, D. Cao, S. Wei, G. Chen, *Macromol. Chem. Phys.* **2014**.
- [67] S. Nazare, B. Kandola, A. Horrocks, *Polym. Adv. Technol.* **2006**, 17, 294.
- [68] H. Gu, J. Guo, Q. He, S. Tadakamalla, X. Zhang, X. Yan, Y. Huang, H. A. Colorado, S. Wei, Z. Guo, *Ind. Eng. Chem. Res.* **2013**, 52, 7718.
- [69] A. Korobko, N. Bessonova, S. Krashenninnikov, E. Konyukhova, S. Drozd, S. Chvalun, *Diamond Relat. Mater.* **2007**, 16, 2141.
- [70] A. G. Simanke, G. B. Galland, L. Freitas, J. A. H. da Jornada, R. Quijada, R. S. Mauler, *Polymer* **1999**, 40, 5489.
- [71] S. Rabiej, B. Goderis, J. Janicki, V. Mathot, M. Koch, G. Groeninckx, H. Reynaers, J. Gelan, A. Włochowicz, *Polymer* **2004**, 45, 8761.
- [72] Q. He, T. Yuan, J. Zhu, Z. Luo, N. Haldolaarachchige, L. Sun, A. Khasanov, Y. Li, D. P. Young, S. Wei, *Polymer* **2012**, 53, 3642.
- [73] Q. He, T. Yuan, X. Zhang, Z. Luo, N. Haldolaarachchige, L. Sun, D. P. Young, S. Wei, Z. Guo, *Macromolecules*, 46, 2357.
- [74] A. Alizadeh, L. Richardson, J. Xu, S. McCartney, H. Marand, Y. Cheung, S. Chum, *Macromolecules* **1999**, 32, 6221.
- [75] W. M. Deen, "Analysis of Transport Phenomena, Topics in Chemical Engineering", Oxford University Press, New York, 1998.
- [76] R. E. Pelrine, R. D. Kornbluh, J. S. Eckerle, Q. Pei, "Electroactive polymer thermal electric generators", Google Patents, 2003.
- [77] L. Zaheed, R. Jachuck, *Appl. Therm. Eng.* **2004**, 24, 2323.
- [78] R. Kumar, D. Molin, L. Young, F. Ke, "New high temperature polymer thin coating for power electronics", in *Applied Power Electronics Conference and Exposition, 2004. APEC'04. Nineteenth Annual IEEE*, IEEE, 2004, p. 2/1247.
- [79] P. Kim, L. Shi, A. Majumdar, P. McEuen, *Phys. Rev. Lett.* **2001**, 87, 215502.
- [80] C. Yu, L. Shi, Z. Yao, D. Li, A. Majumdar, *Nano Lett.* **2005**, 5, 1842.
- [81] A. Moisala, Q. Li, I. Kinloch, A. Windle, *Compos. Sci. Technol.* **2006**, 66, 1285.
- [82] C.-W. Nan, G. Liu, Y. Lin, M. Li, *Appl. Phys. Lett.* **2004**, 85, 3549.
- [83] A. Babel, D. Li, Y. Xia, S. A. Jenekhe, *Macromolecules* **2005**, 38, 4705.
- [84] E. Yablonovitch, G. D. Cody, *Electron Devices, IEEE Transactions on* **1982**, 29, 300.
- [85] M. de la Guardia, *Microchimica Acta* **1995**, 120, 243.
- [86] J. Tauc, *Materials Research Bulletin* **1970**, 5, 721.
- [87] A. Hjelm, C. G. Granqvist, J. M. Wills, *Physical Review B* **1996**, 54, 2436.
- [88] N. Serpone, D. Lawless, R. Khairutdinov, *The Journal of Physical Chemistry* **1995**, 99, 16646.

- [89] M. B. Tzolov, T.-F. Kuo, D. A. Straus, A. Yin, Xu, *The Journal of Physical Chemistry C* **2007**, *111*, 5800.
- [90] J. Wu, W. Walukiewicz, W. Shan, E. Bourret-Courchesne, J. Ager III, K. Yu, E. Haller, K. Kissell, S. M. Bachilo, R. B. Weisman, *Phys. Rev. Lett.* **2004**, *93*, 017404.
- [91] A. M. Smith, S. Nie, *Accounts of chemical research* **2009**, *43*, 190.
- [92] J. D. FAN, Y. M. MALOZOVSKY, *Int. J. Mod Phys B* **2013**, *27*, 1362024.
- [93] O. GÃ¼lseren, T. Yildirim, S. Ciraci, Ã. KÃ¼lÃ¼n, *Physical Review B* **2002**, *65*, 155410.
- [94] L. Yang, M. P. Anantram, J. Han, J. P. Lu, *Physical Review B* **1999**, *60*, 13874.
- [95] Z. H. Ni, T. Yu, Y. H. Lu, Y. Y. Wang, Y. P. Feng, Z. X. Shen, *ACS Nano* **2008**, *2*, 2301.
- [96] Y. Li, J. Zhu, S. Wei, J. Ryu, Q. Wang, L. Sun, Z. Guo, *Macromolecular Chemistry and Physics* **2011**, *212*, 2429.
- [97] S. GD, L. DC, *J. Compos. Mater.* **2009**, *43*, 917.
- [98] L. Hu, D. S. Hecht, G. GrÃ¼ner, *Nano Letters* **2004**, *4*, 2513.
- [99] J. Stejskal, I. Sapurina, M. TrchovÃ¡, J. ProkeÅ, I. Krivka, E. TobolkovÃ¡, *Macromolecules* **1998**, *31*, 2218.
- [100] Z. Guo, K. Shin, A. B. Karki, D. P. Young, R. B. Kaner, H. T. Hahn, *J. Nanopart. Res.* **2009**, *11*, 1441.
- [101] M. Aggarwal, S. Khan, M. Husain, T. Ming, M. Tsai, T. Perng, Z. Khan, *Eur. Phys. J. B* **2007**, *60*, 319.
- [102] B. Hu, Y. Wu, *Nat. Mater.* **2007**, *6*, 985.
- [103] T. A. Skotheim, J. Reynolds, *"Handbook of Conducting Polymers"*, CRC press, 2007.
- [104] R. Rosenbaum, T. Murphy, E. Palm, S. Hannahs, B. Brandt, *Physical Review B* **2001**, *63*, 094426.
- [105] S. Bhadra, D. Khastgir, N. K. Singha, J. H. Lee, *Progress in Polymer Science* **2009**, *34*, 783.
- [106] V. M. Shalaev, *Nature photonics* **2007**, *1*, 41.
- [107] Y. Long, Z. Chen, X. Zhang, J. Zhang, Z. Liu, *Appl. Phys. Lett.* **2004**, *85*, 1796.
- [108] T.-I. Su, C.-R. Wang, S.-T. Lin, R. Rosenbaum, *Physical Review B* **2002**, *66*, 054438.
- [109] Y. Yosida, I. Oguro, *J. Appl. Phys.* **1999**, *86*, 999.

**Chapter 6. Efficient Microwave Solvent-Free Irradiation Synthesis of Highly Conductive
Polypropylene Nanocomposites with Lowly Loaded Carbon Nanotubes**

Abstract

It was well established that microwave radiation was utilized initially to enhance electrical conductivity of carbon nanotube (CNT) polymer nanocomposites (PNCs) without solvent involved. High electrical conductivity was obtained in Polypropylene (PP) nanocomposites with low carbon nanotube (CNT) loading levels. Under inert gas protection, the CNTs were heated through the transformation of electromagnetic energy into mechanical vibrations. The surface of PP was easily melted by the heat generated in the CNT, then a well-formed CNT network was created under a proper microwave treatment period and subsequent hot pressing. The crystalline structures of PNCs, namely crystal structure, crystallization temperature, and crystalline fraction, were obviously affected by the CNT loading level and processing temperature. The electrical conductivity was observed to depend on the pressing temperature and CNT loading level, which are main factors in network formation. A variable range hopping (VRH) mechanistic study revealed a 3-d electron transport mechanism. Unique negative magnetoresistance (MR) phenomena were observed in the PNCs and theoretically analyzed using a forward interference model. The calculated optical band gap of PNCs decreased with increasing CNT loadings. Other properties were tested and analyzed as well.

6.1. Introduction

Microwaves are a form of electromagnetic radiation lying between infrared radiation and radiowaves with wavelengths between 0.001 and 1 m which depend on frequencies between 300 (0.001 m) and 0.3 (1 m) GHz.^[1] Microwaves have wide application in communications, navigation, radar technology, radio astronomy, spectroscopy and heating resource.^[2, 3] In addition, two operating frequencies of microwaves commonly used in industrial, scientific and medical (ISM) applications are 0.915 and 2.450 GHz to avoid interference, which are reserved by the Federal Communications Commission (FCC).^[4] Recently, microwave network analyzers have been allowed to operate at variable frequencies from 0.1 to 20 GHz.^[5]

In 1947, Raytheon built the first commercially available microwave oven. Over the past seven decades, the microwave oven has become an indispensable appliance in most kitchens possessing advantages of faster cooking times and energy saving over conventional cooking methods. Although the utilization of microwaves for heating food is widespread, the application of this technology to process materials is a relatively new development. Multiple benefits to be produced by microwave assisted research contain: reduced processing times, low costs, better production quality, new materials and products, and reduced hazards to humans and the environment health.^[6] Traditional thermal processing is to transfer energy to the materials via convection, conduction, or radiation of heat from the surfaces of materials, which is energy transfer due to thermal gradients. However, microwave energy is transferred directly to materials through molecular interaction, which is the conversion of electromagnetic energy to thermal energy, rather than heat transfer.^[7] Hence, the molecular structure plays an important role in the ability of microwave radiation to interact with materials and energy conversion. When composite or multi-phase materials have diverse dielectric properties, microwave radiation will selectively heat the

material with higher dielectric loss.^[6] Therefore, it is a great advantage to process materials with unique and new microstructures by selectively heating distinct phases. Accordingly, microwave technology acquired fast popularity for processing of metallic, ceramic and polymeric based materials and advanced materials; for instance, metal matrix composites, ceramic matrix composites and polymer matrix composites.^[8-10]

Polymer nanocomposites (PNCs) have gained tremendous impetus as a result of their conspicuous performances arising from their unique and special physicochemical properties, such as low cost, easy processability, light weight, and functional characteristics of nanofillers including outstanding thermal stability, robust flexibility and tunable mechanical, magnetic, rheological and electrochemical properties.^[11-15] In recent fast development of advanced materials, the PNCs with electrical conductivity or semiconductivity have attracted enormous attention due to their wide application, such as energy storage devices,^[16] sensors,^[17-19] kinesiology,^[20-22] aerospace vehicles,^[23] and microwave absorbers.^[24-26] Generally, electrically conductive PNCs are fabricated by mixing conductive nanofillers with the insulating polymer matrix. Among all the conductive nanofillers, carbon nanotubes (CNTs) have generated great expectations for many diverse potential applications for low mass density ^[27], large aspect ratio (typically ca. 300-1000),^[28] good tensile modulus (640 GPa to 1 TPa for single-walled CNTs (SWCNTs)),^[29, 30] and outstanding electrical and thermal conductivities. In particular, the response of CNTs to electromagnetic radiation has been the subject of many investigations. Since strong absorptions are obtained accompanied by intense heating, outgassing and light emission, when CNTs are exposed to microwaves.^[31] In recent years, numerous researchers have used microwaves to purify and functionalize raw CNTs.^[32, 33] However, the microwave irradiation used as a green technology

to prepare highly electrically conductive polymer/CNT nanocomposites as engineering materials has not yet been reported so far.

In this paper, we explored the efficacy of microwave irradiation as an environmentally friendly method for the fabrication of electrically conductive PNCs with lowly loaded CNTs. The formation of CNTs on the surface of PP granules depends on the microwave heating time, and the final electrical conductivity is related to the different processing temperatures. This solvent-free preparation procedure was extremely mild, easy to control, and repeatable. The morphology of the PNCs was investigated by both SEM and TEM. The influence of the CNTs on the EOCs were studied by XRD and DSC. The thermal stability of PNCs was examined by TGA. The rheological behavior of the PNCs, including storage and loss moduli, loss factor, and viscosity were investigated. For all PNCs, the effects of CNT loading level and processing temperature on the electrical conductivity, optical properties, and magnetoresistance were investigated. The electrical conductivity mechanism was theoretically analyzed using a the variable range hopping approach.

6.2. Experiments

6.2.1 Materials

The Polypropylene (PP) used in this study was provided by the Total Company (Total 3270, M_w : 297000, Melt flow rate (MFR): 2.0 g 10min⁻¹, Density: 0.91 g cc⁻¹). The carbon nanotubes (CNTs, SWeNT SMW 200X, average diameter: 10.4 nm; average length: 4.3 μ m) were supplied from SouthWest NanoTechnologies, Inc. All the chemicals were used as-received without any treatment.

6.2.2 Preparation of the nanocomposites

The PP/CNT nanocomposites with 0.15, 0.50, 1.20 and 1.30 wt% CNTs were prepared by microwave solvent-free irradiation as following procedure. As shown in Scheme 1, 125 ml

Buchner flask containing 5 g PP and 2 g CNTs was purged by nitrogen for 15 min, then the vents were sealed by the parafilm immediately. The PP granules were fully surrounded by CNTs after mechanically shaking about 30 s (Vortex-Genie 2, Gear: 6). After that, the PP/CNT mixture was microwaved (Rival 700 Watts) for 5 s as a period; during each interval the mixture was taken out and mechanically shaken for 3 s (Gear: 6). The samples were collected after 4, 5, 6, and 7 periods and marked as 20, 25, 30 and 35 s respectively in this paper. Afterward, the microwave treated mixture was poured into designed container which has ordered pores smaller than granules on the inner wall to collect surplus CNTs (Gear: 8, 3 min). The pure PP was treated as the same procedure without CNTs, which was marked as m_Pure PP. The final pellets were hot pressed into a round disk for testing at 140, 160 and 180 °C to study the effects of the processing temperature on the physical properties of the PNCs.

6.2.3 Characterizations

Differential scanning calorimeter (DSC, TA Instruments Q2000) measurements were implemented under a nitrogen flow rate of approximately 50 mL min⁻¹ at a heating rate of 10 °C min⁻¹. The specimens were first heated from 30 to 200 °C to remove the effect of previous thermal history, cooled down to 30 °C, and reheated again from 30 to 200 °C. The data was collected on the first cooling and second heating processes. The thermal stability of the PP/CNT PNCs was studied by a thermogravimetric analysis (TGA, TA Instruments Discovery). All the samples were heated from 30 to 600 °C under both air and nitrogen atmospheres with a heating rate of 10 °C min⁻¹.

The rheological behavior of the PP/CNT nanocomposites was investigated with a rheometer (TA Instruments Discovery HR-1). An environmental test chamber (ETC) aluminum parallel-plate geometry (25 mm in diameter) was used to perform dynamic rheological

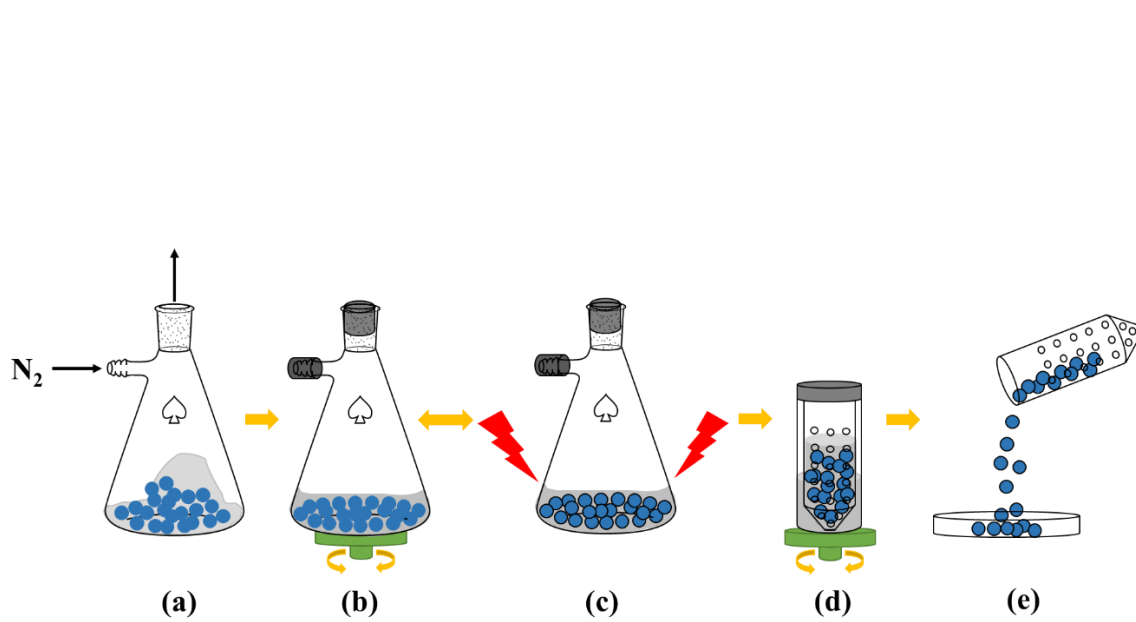
measurements with dynamic oscillation frequency ranging from 0.1 to 100 rad s⁻¹ at a low strain (1.0 %) and the viscosity measurements at shear rates ranging from 0.1 to 100 s⁻¹ at 220 °C. The PP/CNT samples were pressed in the form of disc pellets with a diameter of 25 mm and a average thickness of about 2.0 mm by applying a clamping force of 5 tons in a bench top auto presser (Carver Standard Auto CH).

The crystalline structure of pure PP and its PNCs was studied by X-ray diffraction (XRD), which was carried out using a Bruker AXS D8 ADVANCE diffractometer operating with a Cu K_α radiation source. The X-ray was generated at 45 kV and 40 mA, and XRD scans were recorded at 2θ from 10 to 30° (λ=0.154 nm).

The morphology of the fracture surface of the samples was characterized with a field emission scanning electron microscope (SEM, Zeiss MERLIN). The hot pressed samples were broken in liquid nitrogen for characterization. TEM

UV-vis-NIR diffuse reflectance spectra (DRS) of the PP/CNTs PNCs were recorded on a JASCO spectrophotometer (Model V-670) equipped with a Jasco ISN-723 diffuse reflectance accessory.

The electrical resistivity was measured following a standard four probe method. Magnetoresistance (MR) was carried out using standard four-probe technique by a 9-T Physical Properties Measurement System (PPMS) by Quantum Design at 130 and 290 K.



Scheme 6-1. The procedure of PP/CNT PNCs fabrication by the microwave solvent-free irradiation

6.3. Results and Discussion

6.3.1 Thermal stability

The thermal decomposition curves of pure PP and its PNCs under both nitrogen and air conditions are shown in Figure 6-1a&c, and the corresponding derivative weight loss curves are presented in Figure 6-1b&d, respectively. The CNT loadings of PP/CNT PNCs under different microwave periods are summarized in Table 6-1. The onset (T_{on}) and endset (T_{end}) points are defined as the intersection of an initial tangent line with a final tangent line, which are conducted to determine the points at which changes in the slope of the curve occur. For PNCs under N₂ atmosphere, there is a sharp weight loss stage in the temperature range from 400 to 450 °C, consistent with the observation in He's study,^[34] due to a large scale thermal degradation of PP polymer chains. T_{on} values of CNT/PP PNCs increase slightly with increasing CNT loading, as shown in Table 6-1, which indicates the stabilization of PP by the introduced CNTs. This result also can be proved by DTG curves, in which the peaks of PP/CNT PNCs shift to higher temperatures than that of pure PP (Figure 6-1b). The CNT loadings of PP/CNT PNCs treated under a series of microwave periods can be determined by the TGA curves under N₂ condition, which are 0, 0.15, 0.5, 1.20, 1.30 wt% CNTs for pure PP and 20, 25, 30 and 35 s microwave heating PP/CNT PNCs, respectively.

PP/CNT PNCs with 1.20 wt% CNTs have the highest T_{on} (320.12 °C) under atmosphere condition as shown in Table 6-1, which is about 30 °C higher than that of pure PP. One reason is the strong interfacial particle-polymer interactions.^[35] Another reason is that the heat is absorbed by neat CNTs transitorily to postpone the degradation of PP chains. Since the neat CNTs began to decompose at around 500 °C, which was observed from TGA of neat CNTs in the insert of Figure 6-1c. However, when the CNTs loading reaches 1.30 wt%, the T_{on} decreases slightly due to the

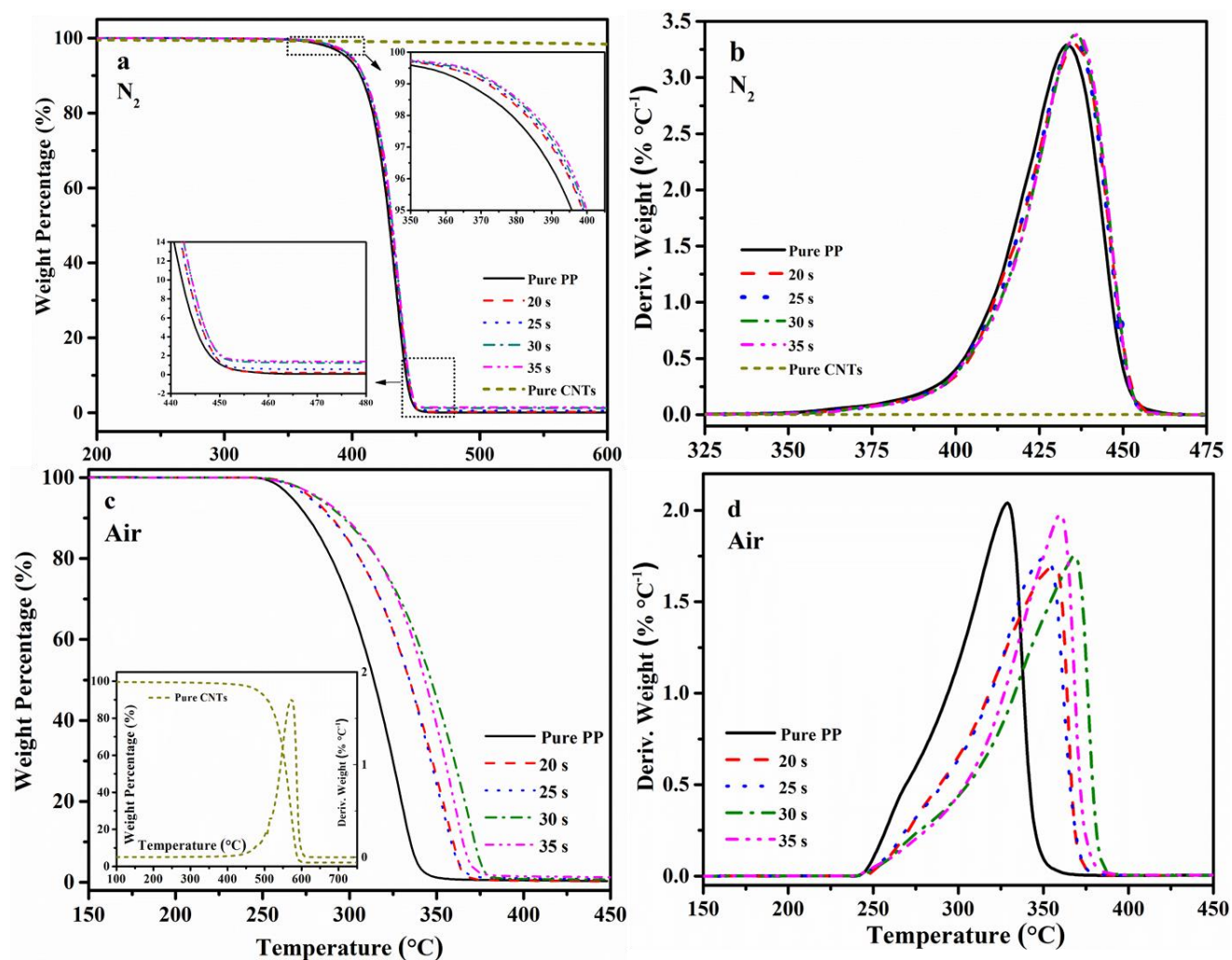


Figure 6-1. Thermogravimetric analysis (TGA) curves of pure PP and its PP/CNT PNCs with 20, 25, 30, 35 s microwave treatment under (a) N_2 and (c) air conditions; and the corresponding derivative thermogravimetric (DTG); Insert in (c): TGA and DTG curves of neat CNTs.

Table 6-1. TGA data of the pure PP and PNCs with CNTs.

		Pure PP	20 s	25 s	30 s	35 s
CNT loading (wt%)		0	0.15	0.50	1.20	1.30
N ₂	T _{on} [°C]	414.26	415.98	416.18	417.10	417.22
	T _{end} [°C]	444.36	445.96	445.62	445.93	446.05
Air	T _{on} [°C]	290.42	306.169	306.27	320.12	319.41
	T _{end} [°C]	339.26	365.121	363.34	377.13	369.31

thermal conductivity of CNTs that can transfer heat to the inner part of the polymer more quickly. The interfacial interaction is destroyed rapidly in the PNCs with increasing the loading of CNTs. The above phenomena also can be obtained in DTG curves, as shown in Figure 6-1d.

6.3.2 Melting and crystalline behaviors

DSC endothermic and exothermic curves revealed the melting and crystallization behaviors of pure PP and its PNCs as shown in Figure 6-2, respectively. The exact crystallization data (crystalline peak temperature, T_c ; enthalpy of the crystallization, ΔH_c ; melting peak temperature, T_m ; enthalpy of the fusion, ΔH_m ; and crystalline fraction, F_c) are summarized in Table 6-2. The ΔH_c and ΔH_m fusion were directly integrated from the DSC curves. For all samples, ΔH_c is smaller than the ΔH_m value, which was attributed to the recrystallization of the samples. The F_c of pure EOCs and nanocomposites can be calculated from Equation (1),^[36]

$$F_c = \frac{\Delta H_m}{\Delta H_m^0 \times (1-x)} \quad (1)$$

where ΔH_m is the enthalpy of the samples (J g^{-1}), ΔH_m^0 is the enthalpy for a theoretical 100% crystalline PP (209 J g^{-1}),^[37] and x is the CNT loading. To study the effects of microwave radiation on the PP granules, the neat (Pure PP) and treated (m_Pure PP) PP granules were compared in Figure 6-2a. The cooling and heating curves of these two samples almost overlap with similar T_c and T_m values, and the F_c also stays unchanged. Therefore, it confirms that the microwave has no influence on pure PP granules after 35 s microwave treatment. Since the pure PP granules have no or negligible energy absorption based on very low dielectric loss factor, they are transparent to microwave energy.^[38]

The microwave treatment duration of PP/CNT PNCs was studied in Figure 6-2b. The T_c values of PP/CNT PNCs are lower than that of pure PP. The variation of T_c is due to different functions of the CNTs during the crystallization process of PP, which can be explained by the spherulitic growth rate (G) as Equation (2) shown:^[39-41]

$$G = G_0 \exp \left[\frac{-U^*}{R(T_c - T_\infty)} \right] \exp \left\{ \frac{-K_g}{[T_c f (T_m^0 - T_c)]} \right\} \quad (2)$$

where G_0 is a factor on the units cm s^{-1} , U^* is the activation energy for the transportation of polymer chain segments to the crystallization sites, R is the gas constant, T_m^0 is the equilibrium T_m , T_c is the crystallization temperature, f is the factor representing the decrease in heat of fusion with decreasing temperature, T_∞ is the hypothetical temperature where all the motions associated with viscous flow ceases, and K_g is the nucleation constant, which can be expressed by Equation 3:^[40]

$$K_g = \frac{4EE_e b_0 T_m^0}{\Delta h_f \rho_c k_B} \quad (3)$$

In the equation, E and E_e are the side and fold surface free energies that measure the work required to create a new surface, b_0 is the single layer thickness, $\Delta h_f \rho_c$ is the enthalpy of melting and k_B is the Boltzmann constant. Hence, the crystallization formation is determined by two parts as shown in Equation 2; the first part contains the contribution of the transport of polymer chain segments to the growth front and the second part is due to the nucleation process. After introducing the CNTs on the surface of pure PP granules, the CNTs would restrain the movement of partial polymer chains to the growth front, which results in a higher U^* value and leads to the crystallization temperature (T_c) shift to a lower value.^[42] However, the CNTs can be served as

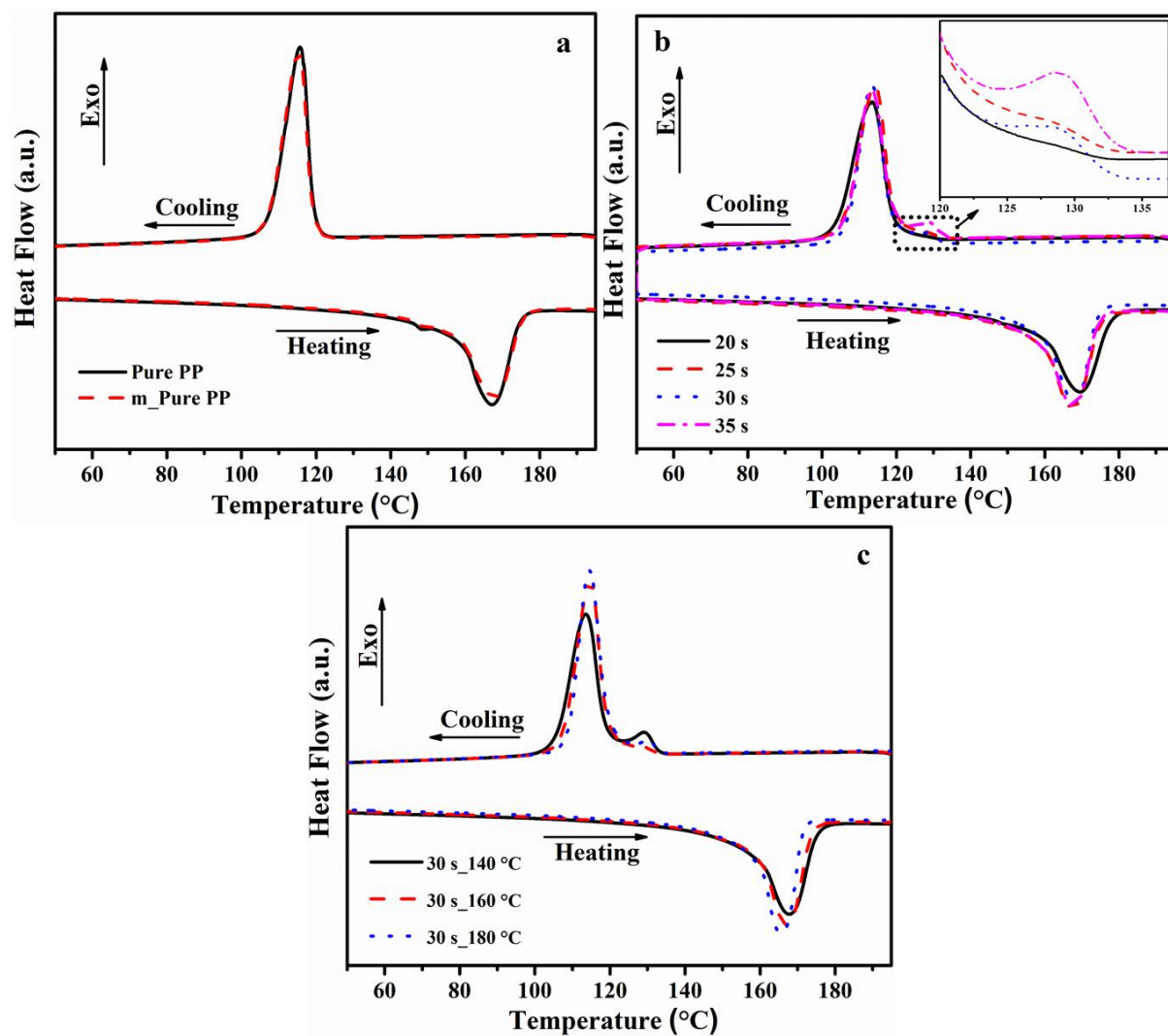


Figure 6-2. DSC curves of a. pure PP granules with (m_Pure PP) and without (Pure PP) 35 s microwave treatment; b. CNTs wrapping PP granules microwave treated by 20 s, 25 s, 30 s and 35 s, respectively; c. CNTs/PP granules with 30 s microwave treatment processed at 140, 160 and 180 °C, respectively.

Table 6-2. DSC Characteristics of pure PP and PNCs with CNTs.

Treatment Time	T_c (°C)	ΔH_c (J g ⁻¹)	T_m (°C)	ΔH_m (J g ⁻¹)	F_c (%)
Pure PP	115.71	154.0	167.33	124.2	59.43
m_Pure PP	115.19	154.2	167.70	124.0	59.33
20 s	113.38	151.0	169.45	130.6	62.58
25 s	114.29	150.7	168.55	131.0	62.99
30 s	113.36	150.2	168.14	132.1	63.97
35 s	113.29	151.8	167.88	133.8	64.86
30 s_140°C	113.55	151.4	167.81	127.6	61.79
30 s_160°C	114.69	152.9	167.22	129.3	62.62
30 s_180°C	114.70	153.6	165.59	129.4	62.67

nucleation sites and foster the crystallization of PP by reducing the surface free energy barrier towards nucleation, thus the crystallization of PP/CNT PNCs under 25 s microwave treatment with 0.5 wt% CNTs was initiated at slightly higher temperature.^[43] In addition, a small shoulder can be obtained in the PNCs with 1.20 and 1.30 wt% CNTs. However, pure PP and PNCs with 0.15 and 0.50 wt% CNTs have no shoulder during the crystallization process. The separation of crystallization peaks depicts a variation of the crystal structures. Both α and γ phases of PP were formed during crystallization, the γ phase can be formed with a lower supercoolings. During the cooling proceeding, γ phase PP would firstly form dominant lamellae and the α phase would grow on it.^[44] Thus, the small shoulder is due to the formation of γ phase PP and the CNTs promotes the γ phase PP.

In order to study the effects of hot pressing process temperature on PP/CNT PNCs, PNCs treated by 30 s microwave and hot pressed at 140, 160 and 180 °C were investigated in Figure 6-2c. From the data summarized in Table 6-2, F_c increases slightly after introducing CNTs into the hosting PP. The higher F_c of these PNCs is owing to the higher process temperature, which promotes the crystalline structure formation of the PP chains.

6.3.3 Crystallinity

The effects of the CNT loading and processing temperature on the crystal structure of pure PP and its PNCs were examined by XRD. PP possesses a noteworthy complexity of crystal structures, including α , β and γ phases, though the simplicity of its chemical structure. Each of α , β and γ phase shows its own characteristic peaks in the XRD patterns. As presented in Figure 6-3, the peak intensity of pure PP increases gradually with increasing processing temperature, which is concordant with Zanneti's results.^[45] However, the peak intensity of PP/CNT PNCs with 35 s microwave heating increases firstly at 160 °C, then both peak intensity and crystal structures

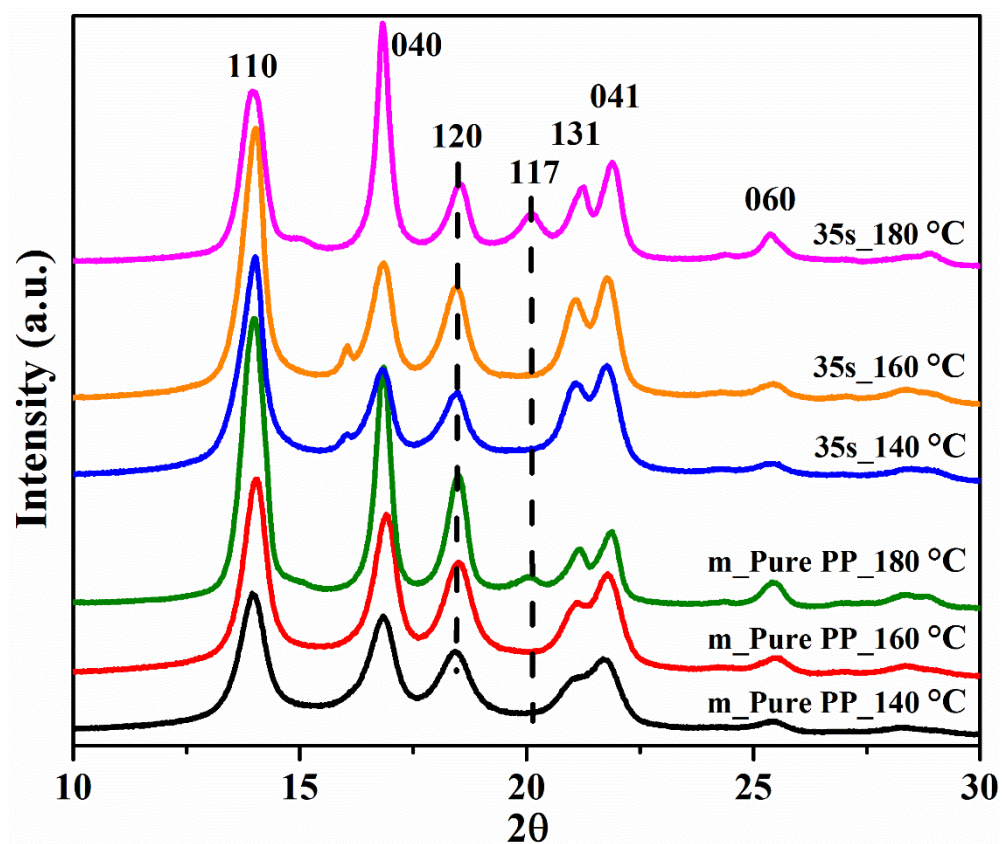


Figure 6-3. X-ray diffraction patterns of pure PP and 35 s microwave heating PP/CNT PNCs processed at 140, 160 and 180 °C.

undergo changes when processing temperature reaches to 180 °C. The intensity of the (040) peak is stronger than that of the (110) peak, and the characteristic peak of γ phase was obtained at $2\theta = 20.09^\circ$. The peaks at $2\theta = 14.04, 16.85, 21.13, 21.92$ and 20.50° correspond to the (110), (040), (131), (041) and (060) crystalline planes of α -PP, respectively. The α phase is usually determined from the peak $2\theta = 18.50^\circ$ corresponding to the 120 crystalline plane.^[46] To explore the effects of CNTs on the crystalline phase of PP, the amount of γ phase PP (X_γ) can be calculated by Equation (4):^[47]

$$X_\gamma = h_\gamma / (h_\gamma + h_\alpha) \quad (4)$$

where h_α and h_γ are the peak height at $2\theta = 18.50$ and 20.09° for the (120) and (117) peak, respectively. The values of X_γ were 0.1197 and 0.3676 for pure PP and 35 s microwave heating PP/CNT PNCs pressed at 180 °C, respectively. Compared with pure PP, the PNCs with 35 s microwave exhibit more amount of γ phase PP, confirming that the CNTs promoted the γ phase PP formation.

6.3.4 Melt Rheological Behavior

Different melting rheological behavior of PNCs plays a very important role in evaluating the internal structure of materials, including the fillers dispersion, aspect ratio, orientation of fillers, and the interaction between fillers and the polymer matrix.^[48] Figure 6-5(a-c) present the storage modulus (G'), loss modulus (G'') and loss factor ($\tan\delta$) of the pure PP and its PNCs processed at 180 °C as a function of angular frequency (ω). The PP chains are fully relaxed and revealed typical homogeneous polymer-like terminal behavior. G' is relatively widely separated in the low frequency range, which is attributed to the increased solid-like behavior of the PNCs after introducing CNTs. The similar phenomena is also obtained in the PP/MWCNT (multi-walled

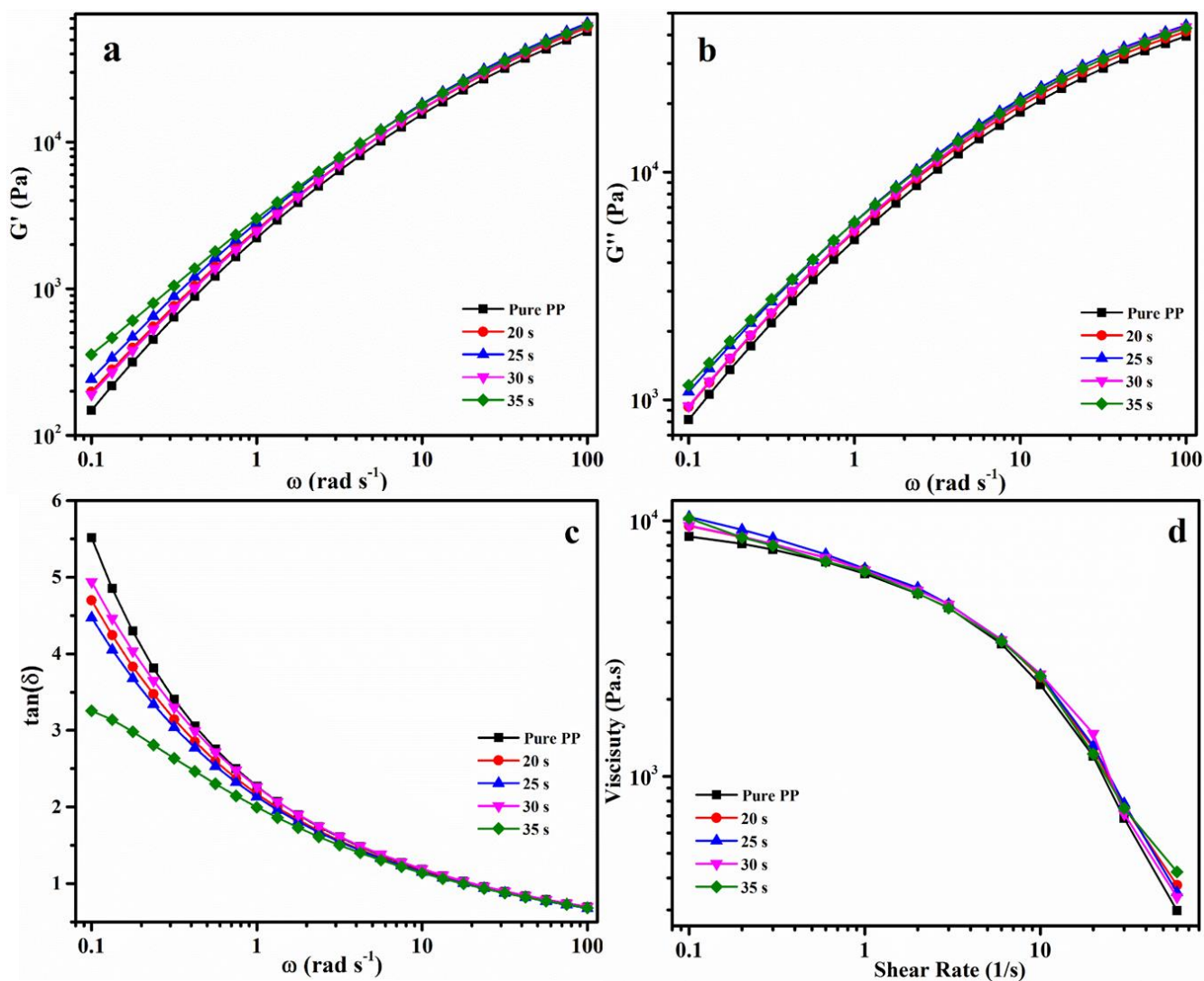


Figure 6-4. (a) Storage modulus (G'), (b) loss modulus (G''), (c) loss factor ($\tan \delta$) vs. angular frequency (ω) and (d) Viscosity vs. shear rate of pure PP and PP/CNT nanocomposites with different time microwave treatment processed at 180 °C.

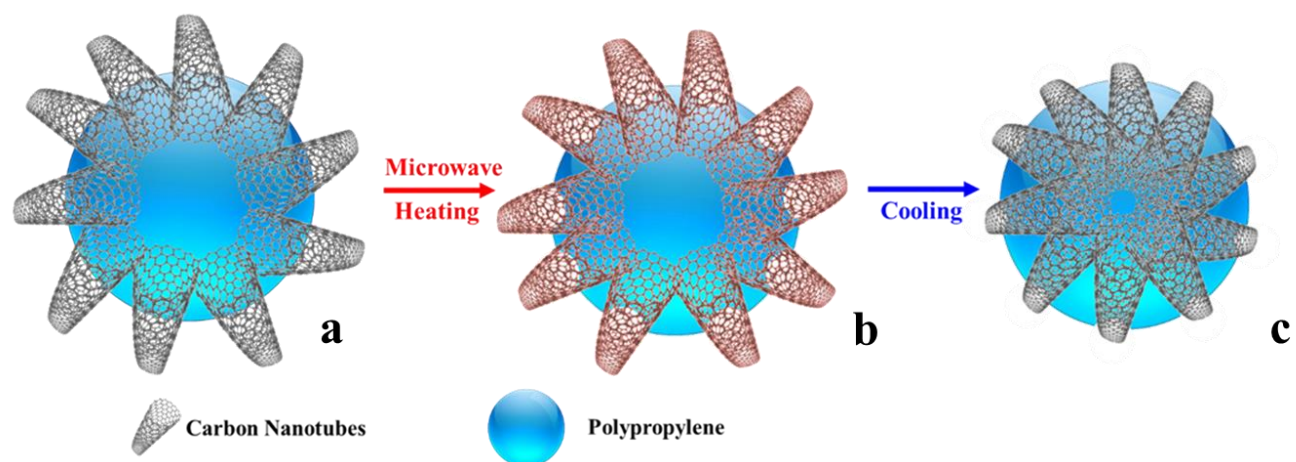
carbon nanotube) PNCs prepared by diluting highly concentrated masterbatch chips.^[49] However, the effect of the CNT loading on the viscoelastic properties (G' , G'' and $\tan \delta$) of PNCs is relatively weak at high frequencies, revealing that the CNTs are not affecting the short-range dynamics of the PP chains.^[50] In addition, the G'' curve has a similar tendency, linearly increasing with increasing frequency. The $\tan \delta$ (the ratio of G'' to G') is employed to characterize the damping property of the PNCs. The $\tan \delta$ value of pure PP is larger than that of PP/CNT PNCs. Since the polymer chain relaxation and relative motion of PP/CNT PNCs are hardly restrained by the existing CNTs, which results in less internal chain-chain friction heat generated in PNCs after applying the same oscillation frequency than that in pure PP. The viscosity as a function of shear rate of pure PP and its PNCs was also studied in Figure 6-5d. All these samples did not present a Newtonian plateau and showed shear thinning behavior in the melt state, which displayed decreasing viscosity with increasing shear rate.^[51] The alignment of the CNTs is destroyed by random thermal motion. Meanwhile, the rebuilding of the polymer chain entanglement is slower than breaking the physically cross-linked sites with increasing the shear rate. The viscosity of the PNCs with the incorporation of CNTs slightly larger than that of pure PP, which results in the increased melt free volume growing after adding nanoparticles in the entangled and confined systems ($h < R_g$, h is the average interparticle half-gap; R_g is the polymer gyration radius), and the mobility of polymer chains was restrained due to the dilution effect from nanoparticles.^[52] The stronger shear thinning behavior was also observed in PP/CNT PNCs made by the masterbatch dilution method.^[53]

6.3.5 Formation Mechanism of PP/CNT PNCs

A fundamental understanding of the reciprocity of materials with microwave irradiation is the key to develop the technology for widespread use. The mechanism of PP/CNT PNCs prepared

by microwave irradiation was presented in Scheme 6-2. The PP granules were fully covered by CNTs in an inert atmosphere. Based on electrostatic forces, the PP granules were also wrapped by light CNTs as shown in Scheme 6-2a. With the action of the microwave on the CNTs and polymer mixture, heat was generated in CNTs without any effects on PP granules as presented in Scheme 2b. Then, the temperature of CNTs is controlled high enough to melt the surface of PP granules without the polymer decomposition by proper heating period. To prepare homogenously coating materials, the regular shake of mixture is necessary since the microwave resource was localized. Consequently, the CNTs were stuck on the PP granules surface and form a network as shown in Scheme 6-2c.

The heat caused by microwave irradiation can be explained by two main factors as conduction (Joule heating) and dipolar polarization. Normally, different impurities can be obtained in commercially available CNTs, such as carbon and metals, which are electrically conductive and can support the mechanism based on conduction heating. In this mechanism, the microwaves make the electrons move by an electric field, causing sample heating instead of heating the material immediately. In this way, the metal catalyst particles should cause localized superheating by inducing Joule heating.^[54] Moreover, the extended π -system allows conductivity (and thus Joule heating) to enable localized heating.^[55] Meanwhile, the generation of gas plasma from absorbed gases (in particular, H_2) in CNTs under microwave radiation should be considered as another potential way of localized superheating.^[31] The dipolar polarization also has a contribution to imperfect CNT microwave heating due to the structural imperfections of as-synthesized CNTs, which cause the decay of ballistic transport, which results in Joule heating representing as superheating.^[56] In 2006, Ye *etc.* proposed a simple model to explain microwave-induced heating



Scheme 6-2. The mechanism of PP/CNT PNCs fabrication via microwave irradiation.

of CNTs describing the transformation of electromagnetic energy into mechanical vibrations.[57] This model emphasized that a transverse parametric resonance causes the CNTs to undergo superheating, which is a consequence of the polarization of the CNTs exposed to microwave radiation.

6.3.6 Electrical Conductivity (σ) of PP/CNT Nanocomposites

The conductivity (σ) of the pure PP and its PNCs processed at different temperatures as a function of the CNT loadings is shown in Figure 6-7. The σ ($\sim 10^{-9}$) of pure PP was acquired from the literature.^[58] It was observed that σ elevated with increasing the CNT loadings, and the PNCs with 1.30 wt% CNTs processed at 160 °C showed the highest σ of 0.46 S cm⁻¹. Recently, Wu *et al.* reported that σ of PP/MWCNT composites can reach $\sim 10^2$ S cm⁻¹ with 10 wt% MWCNTs prepared by a mixing method. However, σ is less than $\sim 10^{-6}$ S cm⁻¹, when the composites contained ~ 2 wt% MWCNTs.^[59] Compared with materials fabricated by conventional methods, the higher σ found in this study is attributed to the well-formed conductive CNT network with the advantages of microwave heating and processing temperature. With different microwave heating periods, the PP/CNT PNCs were coated with different weights of CNTs, which was already proved by TGA. As shown in Scheme 6-3(a), at 140 °C, the PP pellets have a tendency to melt. The pellets could only change shape without destroying the CNT layer in the hot press process; however, the interaction between each pellet is too weak to make the CNT layers combine together. As marked red arrows in Figure 6-6a, a gap can be obtained between two pellets coated with CNTs, which arises from the lower mobility of both CNTs and PP chains at 140 °C. That is the reason why PP/CNT PNCs processed at 140 °C have the lowest σ at each nanofiller content. At 160 °C, the pellets were in the molten state, and the interactions of the pellets is enhanced by easier movement

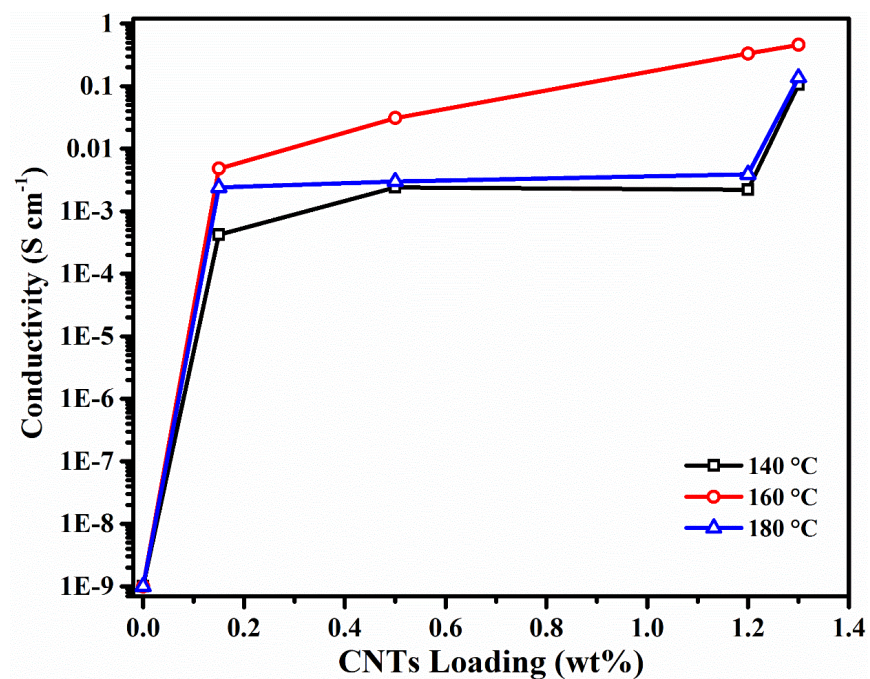
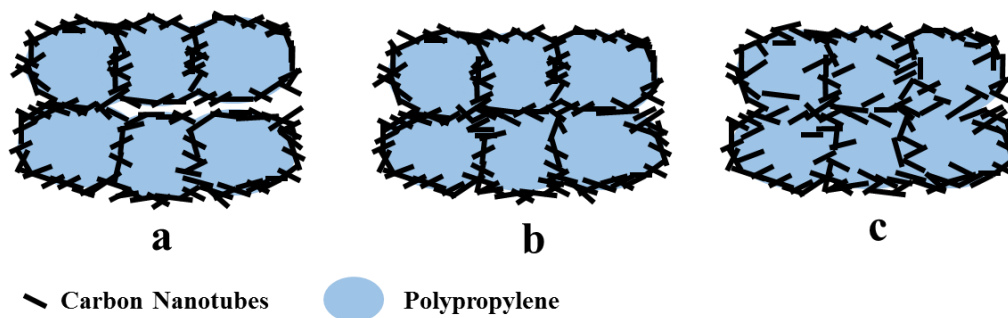


Figure 6-5 Electrical conductivity (σ) of PNCs vs CNTs weight loading for the samples processed at 140, 160 and 180 °C.



Scheme 6-3. Morphology of PNCs with CNTs at different processing temperature

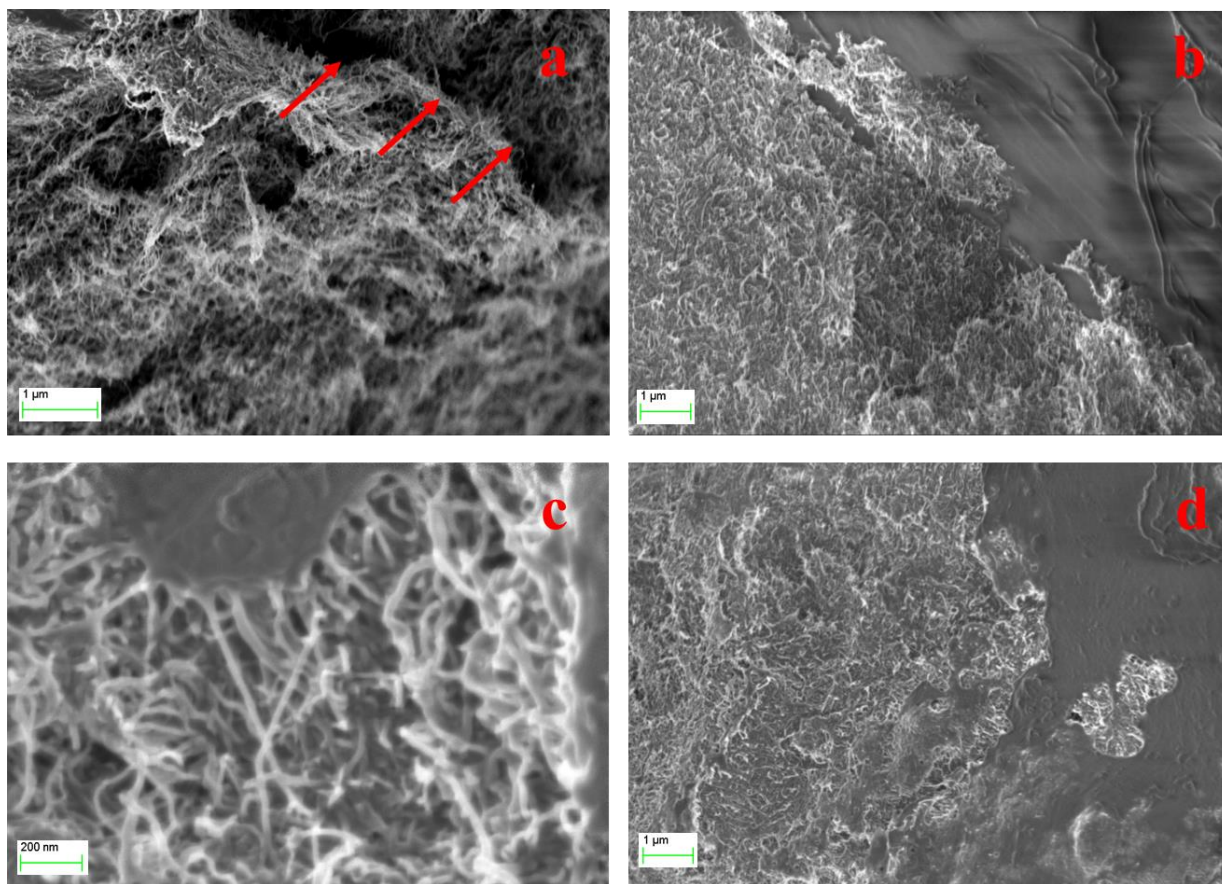


Figure 6-6. SEM microstructures of PP/CNT PNCs with (a) 25 s microwave treatment prepared at 140 °C, (b) 20 s microwave treatment prepared at 160 °C, and 35 s microwave treatment prepared at (c) 160 and (d) 180 °C.

of CNTs and PP chains, which results in CNT layers forming a tight network, as presented in Scheme 6-3(b). That can be confirmed by Fig 6-6b, in which the CNTs cling more closely on the surface of PNCs than those shown in Fig 6-6a. The higher processing temperature leads to less resistance of molecular motions and strong interactions between the nanofiller and polymer chains.^[60] Moreover, with longer microwave treatment, a better network was constructed as shown in Fig. 6-6c. The PP/CNT PNCs processed at 160 °C have the highest σ and remain an uptrend. The electrons could hop from one nanotube to an adjacent one in the formed CNT network structure, which results in the enhancement of the electrical conductivity.^[61] However, when the temperature reaches 180 °C, σ became lower, owing to the reduced density of the CNTs network, even the network of CNTs was broken, as viewed in Scheme 6-3(c). The PNCs were totally molten at 180 °C, allowing molecules to move continually. Thus, more CNTs were released from the layers. From Figure 6-6d, the PP surface became flatter and the CNT coating layer was separated by PP because of the molten matrix, which limited the number of CNTs that can join in the conductive path formation.

6.3.7 Electrical Conductivity Mechanism

The resistivity as a function of temperature for PNCs with 20 s microwave treatment prepared at 180 °C, 30 s microwave treatment prepared at 160 °C, and 35 s microwave treatment prepared at 140 and 180 °C is presented in Figure 6-7. The resistivity decreases with increasing temperature for all samples, depicting a semiconducting behavior within the 50-290 K temperature range.^[62] The resistivity is found to follow the variable range hopping (VRH) theory, which is related with the network structure in the polymer matrix. To explore the electron transportation

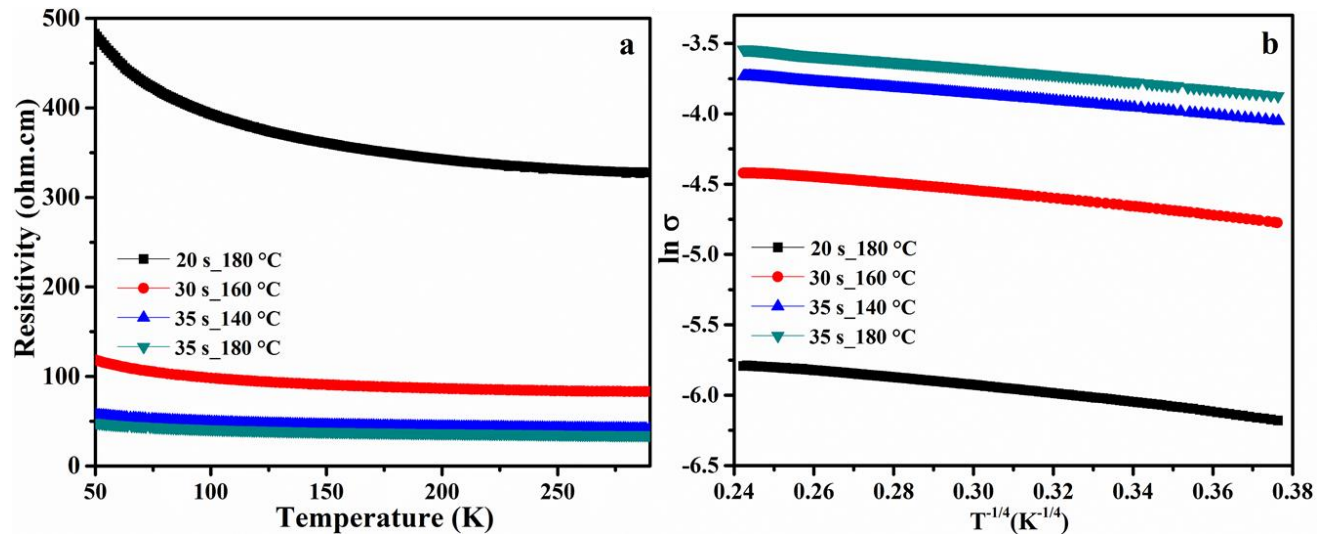


Figure 6-7. a) Resistivity vs temperature and b) $\ln(\sigma)$ vs $T^{-1/4}$ curves of CNTs PNCs.

Table 6-3. T_0 and σ_0 for CNT PNCs.

Samples	T_0 (K)	σ_0 (S cm ⁻¹)
20 s_180 °C	43.50	0.0058
30 s_160 °C	40.78	0.0227
35 s_140 °C	17.02	0.0390
35 s_180 °C	22.21	0.0486

mechanism of the PNCs, the VRH relationship between σ and temperature was investigated using Equation (7),^[63]

$$\sigma = \sigma_0 \exp \left[- \left(\frac{T_0}{T} \right)^{1/(n+1)} \right], n = 1, 2, 3 \quad (5)$$

where the constant T_0 (K) is the characteristic Mott temperature, depending on the electronic wave function localization degree, the constant σ_0 is the electrical conductivity at infinitely low temperature, T (K) is the Kelvin temperature, and n can be equal to 1, 2 and 3, meaning for one-, two-, and three-dimensional systems, respectively. The best linear fits of $\ln(\sigma) \sim T^{-1/(n+1)}$ for PNCs calculated from Figure 6-7a are shown in Figure 6-7b with $n = 3$ in 50 - 290 K temperature range, revealing a 3-d electron transport mechanism. T_0 and σ_0 values can be gained from the intercept and the slope of the plot $\ln(\sigma) \sim T^{-1/(n+1)}$ summarized in Table 6-3. The variation of the T_0 and σ_0 values is associated with the electrical conductivity mechanism of the composites. The T_0 value of PP/CNT PNCs is observed to obey the order consistent with the measured resistivity values. Generally, a larger T_0 indicates a stronger localization of the charge carriers in the system and thus leads to a lower σ .^[64] The σ_0 value increases with elevating CNT loading, and at the same CNT loading, the σ_0 value depends on the processing temperature. The PP/CNT PNCs with 20 s microwave heating remain relatively low in the number of CNTs; thus the CNT layer was easily destroyed by PP at 180 °C. Then the charge transport was partitioned and caused a higher T_0 and lower σ_0 .

6.3.8 Electronic Property of CNT/ PP Nanocomposites

CNTs possess a number of unique and special properties that signify great promise for nanoelectronics applications. The band gap is the most significant property in designing CNTs for

electronics applications.^[65] The optical properties of pure CNTs and PNCs were studied by the ultraviolet-visible (UV-vis) spectra, as shown in Figure 6-8. The band gap (E_g) values can be calculated from a photon-energy ($h\nu$) dependence of $\alpha h\nu$ converted from the diffuse reflectance UV-Vis spectra by Tauc's plot, as in Equation (6),^[66]

$$\alpha h\nu = (h\nu - E_g)^n \quad (6)$$

where α , h and ν are the absorbance coefficient, Planck's constant and the photon frequency, respectively. The Tauc plot was converted from the diffuse reflectance UV-vis spectra. The parameter n is a pure number associated with different types of electronic transitions. $n = 1/2$ is for the allowed direct (the minimum energy level of the lowest conduction band positioned directly under the maximum of the highest valence band in k space), and $n = 2$ is for the allowed indirect (the minimum energy level of the lowest conduction band is shifted relative to the maximum of the highest valence band, and the lowest-energy interband transition must then be accompanied by phonon excitation) transitions).^[67, 68] The reported n is ~ 2 ^[69] for CNTs and the E_g was calculated by extrapolating from the energy axis in the linear portion of the curve. The calculated E_g of pure CNTs is ~ 1.50 eV, which is comparable to the 1.543 eV reported for the transition above the second pair of van Hove singularity and below the Fermi level of CNTs with an index of (9,8).^[70] For all the PNCs, the E_g values are higher than those of pure PP. The changing trend of E_g corresponds to the σ values in the PNCs; the PNCs with higher σ showed a lower E_g . To study the effects of processing temperature on the E_g , the E_g values of pure CNTs and PP/CNT PNCs with 35 s microwave heating processed at different temperatures can be observed in Figure 6-8b. The lower E_g is obtained in a certain CNT loading PNCs processed at 160 °C. The variation of E_g can be interpreted from the strain of the CNTs, which was joined during the hot press process. Since the CNT strain could have a positive or negative effect on the electron transportation in the CNTs.

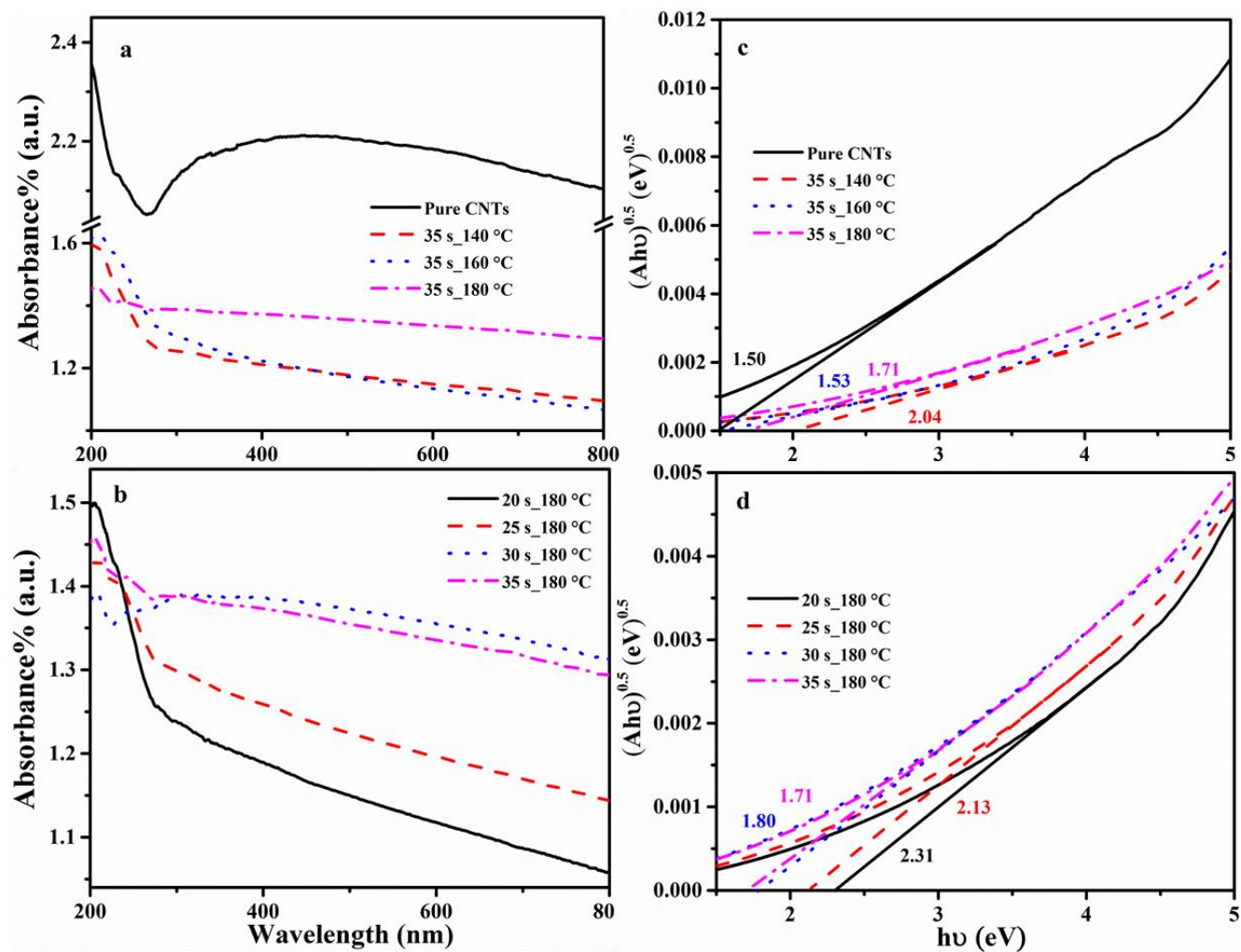


Figure 6-8. (a & b) UV-vis absorbance spectra and corresponding (c & d) Tauc polts converted from diffuse reflectance spectra data, respectively.

The uniaxial or torsional strain can lead to the insulator-metal transition of SWNT arising from the varied quantum number.^[71, 72] However, uniaxial strain in graphene causes the red shift of the 2D and G band arising from the elongation of the C-C bonds.^[73] For the PP/CNT system, the E_g decreases with increasing the CNT loading as presented in Figure 6-8d. The σ takes place arising from the existing electrons in the delocalized states. One orbital must be partially filled with electrons; however, the orbital is inert to block the transport of other electrons when fully filled. Partially filled states and the state delocalization led to a lower E_g due to the formed network of CNTs.

6.3.9 Magnetoresistance (MR)

Figure 6-9 shows the magnetoresistance (MR) of PNCs with 30 s microwave treatment processed at 160 °C as measured at 290 K, respectively. The MR can be calculated using Equation (7),^[74]

$$\text{MR}\% = \frac{R(H, T) - R(0, T)}{R(0)} \times 100 \quad (7)$$

where $R(0, T)$ is the resistance without magnetic field and $R(H, T)$ is the resistance under a magnetic field H . The MR results reveal different magnetic field dependent behavior that can be divided into positive and negative groups. The positive MR is owing to the shrinkage in the overlap of electron wave functions after applying a magnetic field, and thus the average hopping length reduced.^[75] The orbital magnetoconductivity theory is utilized to studied the negative MR effect, which considered the effects of interference among various hopping paths.^[76] For PNCs with 30 s microwave treatment measured at 290 K, a linear negative MR was observed at low magnetic field strength. Furthermore, the materials were saturated at high magnetic fields. In orbital magnetoconductivity theory, these hopping paths include a sequence of scattering of tunneling

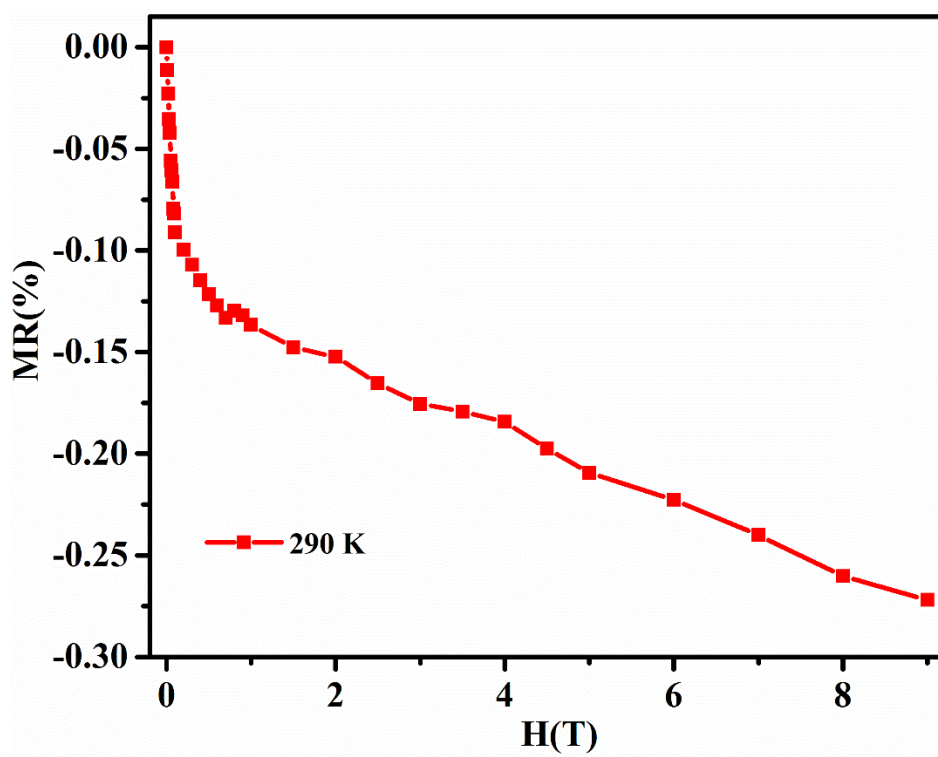


Figure 6-9. Magnetoresistance of PNCs with 30 s microwave treatment processed at 160 °C characterized at 290 K, respectively.

electrons by the impurities located within a cigar-shaped domain of length r_h (hopping distance) and width $(r_h a_0)^{1/2}$.^[77] The ratio $R(H,T)/R(0,T)$ arising from interference effects is presented by empirical Equation (8).^[78]

$$R(H,T)/R(0,T) \approx 1/[1 + C_{sat} [H/H_{sat}]/[1 + H/H_{sat}]] \quad (8)$$

where the fitting parameter is constant and also named temperature independent fitting parameter and H_{sat} is effective saturation magnetic field. According to the Mott VRH electrical conduction mechanism, H_{sat} can be calculated by Equation (8):^[77, 79]

$$H_{sat} \approx 0.7 \left(\frac{8}{3}\right)^{3/2} \left(\frac{1}{a_0^2}\right) \left(\frac{h}{e}\right) \left(\frac{T}{T_0}\right)^{3/8} \quad (9)$$

where h is the Planck's constant, T_0 is the Mott characteristic temperature (K). In the low-field limit, Equation (9) can be transformed to Equation (10):

$$R(H,T)/R(0,T) \approx 1 - C_{sat} [H/H_{sat}] \quad (10)$$

Substituting Equation (9) into Equation (10) and rearranging, the MR can be calculated from Equation (11):

$$MR = \frac{R(H,T) - R(0,T)}{R(0,T)} \approx -C_{sat} [H/H_{sat}] = -C_{sat} \frac{H}{0.7 \left(\frac{8}{3}\right)^{3/2} \left(\frac{1}{a_0^2}\right) \left(\frac{h}{e}\right) \left(\frac{T}{T_0}\right)^{3/8}} \quad (11)$$

The calculated a_0 of PNCs with 1.20 wt% CNTs measured at 290 K are 636.75, 495.37, and 416.120 nm at H of 2, 4, and 8 T, respectively. The a_0 values decrease with increasing H , due to the increase in polaron population at the expense of bipolarons with increasing magnetic field strength.^[80] The negative MR is also obtained in a nanoporous system composed of bundles of single-walled carbon nanotubes (SWCNTs).^[81] The lower measured temperature causes a reduced resistance of CNT network, resulting in a negative MR.

6.4. Conclusions

Microwave radiation can be used for heating materials selectively. Highly electrically conductive PP/CNT PNCs were successfully synthesized by an efficient microwave solvent-free irradiation method under inert atmosphere and controlled treatment time. This method gives a new perspective for designing CNT based conductive polymer materials on an industrial scale with environment-friendly technology. No effects of microwave radiation on PP granules lasting 35 s were confirmed. The thermal stability of CNT/PP PNCs can be enhanced under both air and N₂ conditions. A strong interaction between the CNTs and the polymer matrix led to less frictional heat loss in the PNCs than that of pure PP. Both XRD and DSC results depicted that higher processing temperature promoted the formation of γ -phase PP. The morphology study showed that CNT network structure depended on the processing temperature. Well-formed CNT networks resulted in higher electrical conductivity, and the electrical conductivity mechanism stayed within a 3 dimension variable range hopping. The changing trend of the E_g value of the PNCs followed the electrical conductivity value of the PNCs, implying that PNCs with higher conductivity showed a lower E_g . Negative MR can be observed in PNCs with 1.20 wt% CNTs measured at 290 K, providing a promising approach to design desired MR devices.

6.5. References

- [1] W. C. Jakes, D. C. Cox, "Microwave mobile communications", Wiley-IEEE Press, 1994.
- [2] M. I. Skolnik, **1970**.
- [3] A. a. Metaxas, R. J. Meredith, "Industrial microwave heating", IET, 1983.
- [4] R. J. Meredith, "Engineers' handbook of industrial microwave heating", IET, 1998.
- [5] Q. He, T. Yuan, X. Zhang, X. Yan, J. Guo, D. Ding, M. A. Khan, D. P. Young, A. Khasanov, Z. Luo, *The Journal of Physical Chemistry C* **2014**, *118*, 24784.
- [6] E. Thostenson, T.-W. Chou, *Composites Part A: Applied Science and Manufacturing* **1999**, *30*, 1055.
- [7] D. E. Clark, D. C. Folz, J. K. West, *Materials Science and Engineering: A* **2000**, *287*, 153.
- [8] D. K. Agrawal, *Current Opinion in Solid State and Materials Science* **1998**, *3*, 480.
- [9] L. Zong, S. Zhou, N. Sgriccia, M. Hawley, L. Kempel, *The Journal of microwave power and electromagnetic energy: a publication of the International Microwave Power Institute* **2002**, *38*, 49.
- [10] S. Singh, D. Gupta, V. Jain, A. K. Sharma, *Materials and Manufacturing Processes* **2015**, *30*, 1.
- [11] X. Guan, G.-Q. Zheng, K. Dai, C. Liu, X. Yan, C. Shen, Z. Guo, *ACS applied materials & interfaces* **2016**.
- [12] H. Zhao, X. Yan, G. Zhao, Z. Guo, *Polymer Engineering & Science* **2016**.
- [13] L. Zhang, Y. Qin, G. Zheng, K. Dai, C. Liu, X. Yan, J. Guo, C. Shen, Z. Guo, *Polymer* **2016**, *90*, 18.
- [14] S. Guo, J. Liu, S. Qiu, Y. Wang, X. Yan, N. Wu, S. Wang, Z. Guo, *Electrochimica Acta* **2016**, *190*, 556.
- [15] X. Yan, Q. He, X. Zhang, H. Gu, H. Chen, Q. Wang, L. Sun, S. Wei, Z. Guo, *Macromolecular Materials and Engineering* **2014**, *299*, 485.
- [16] A. S. Aricò, P. Bruce, B. Scrosati, J.-M. Tarascon, W. Van Schalkwijk, *Nature materials* **2005**, *4*, 366.
- [17] J. Zhu, H. Gu, Z. Luo, N. Haldolaarachige, D. P. Young, S. Wei, Z. Guo, *Langmuir* **2012**, *28*, 10246.
- [18] H. Gu, J. Guo, H. Wei, Y. Huang, C. Zhao, Y. Li, Q. Wu, N. Haldolaarachchige, D. P. Young, S. Wei, *Physical Chemistry Chemical Physics* **2013**, *15*, 10866.
- [19] H. Gu, J. Guo, X. Zhang, Q. He, Y. Huang, H. A. Colorado, N. Haldolaarachchige, H. Xin, D. P. Young, S. Wei, *The Journal of Physical Chemistry C* **2013**, *117*, 6426.
- [20] L. J. Lee, C. Zeng, X. Cao, X. Han, J. Shen, G. Xu, *Composites science and technology* **2005**, *65*, 2344.
- [21] R. Rahimi, M. Ochoa, W. Yu, B. Ziaie, *ACS applied materials & interfaces* **2015**, *7*, 4463.
- [22] M. Amjadi, A. Pichitpajongkit, S. Lee, S. Ryu, I. Park, *ACS nano* **2014**, *8*, 5154.
- [23] J. Njuguna, K. Pielichowski, *Advanced Engineering Materials* **2003**, *5*, 769.
- [24] J. Zhu, S. Wei, N. Haldolaarachchige, D. P. Young, Z. Guo, *The Journal of Physical Chemistry C* **2011**, *115*, 15304.
- [25] Z. Guo, S.-E. Lee, H. Kim, S. Park, H. Hahn, A. Karki, D. Young, *Acta Materialia* **2009**, *57*, 267.
- [26] Z. Guo, S. Park, H. T. Hahn, S. Wei, M. Moldovan, A. B. Karki, D. P. Young, *Journal of applied physics* **2007**, *101*, 09M511.
- [27] G. Gao, T. Cagin, W. A. Goddard III, *Nanotechnology* **1998**, *9*, 184.

- [28] X. Wang, Q. Li, J. Xie, Z. Jin, J. Wang, Y. Li, K. Jiang, S. Fan, *Nano letters* **2009**, 9, 3137.
- [29] L. Sun, G. Warren, J. O'reilly, W. Everett, S. Lee, D. Davis, D. Lagoudas, H.-J. Sue, *Carbon* **2008**, 46, 320.
- [30] T. Uchida, S. Kumar, *Journal of applied polymer science* **2005**, 98, 985.
- [31] T. Imholt, C. A. Dyke, B. Hasslacher, J. M. Pérez, D. Price, J. A. Roberts, J. Scott, A. Wadhawan, Z. Ye, J. M. Tour, *Chemistry of materials* **2003**, 15, 3969.
- [32] P.-X. Hou, C. Liu, H.-M. Cheng, *Carbon* **2008**, 46, 2003.
- [33] A. de la Hoz, A. Diaz-Ortiz, A. Moreno, *Chemical Society Reviews* **2005**, 34, 164.
- [34] Q. He, T. Yuan, X. Yan, D. Ding, Q. Wang, Z. Luo, T. D. Shen, S. Wei, D. Cao, Z. Guo, *Macromolecular Chemistry and Physics* **2014**, 215, 327.
- [35] X. Yan, M. Li, J. Long, X. Zhang, H. Wei, Q. He, D. Rutman, D. Cao, S. Wei, G. Chen, *Macromolecular Chemistry and Physics* **2014**.
- [36] Q. He, T. Yuan, X. Zhang, Z. Luo, N. Haldolaarachchige, L. Sun, D. P. Young, S. Wei, Z. Guo, *Macromolecules*, 46, 2357.
- [37] A. T. Jones, J. M. Aizlewood, D. Beckett, *Die Makromolekulare Chemie* **1964**, 75, 134.
- [38] D. E. Clark, W. H. Sutton, *Annual Review of Materials Science* **1996**, 26, 299.
- [39] J. D. Hoffman, R. L. Miller, H. Marand, D. B. Roitman, *Macromolecules* **1992**, 25, 2221.
- [40] G. Z. Papageorgiou, D. S. Achilias, D. N. Bikiaris, G. P. Karayannidis, *Thermochimica Acta* **2005**, 427, 117.
- [41] H. Tsuji, H. Takai, S. K. Saha, *Polymer* **2006**, 47, 3826.
- [42] J. Zhu, S. Wei, Y. Li, L. Sun, N. Haldolaarachchige, D. P. Young, C. Southworth, A. Khasanov, Z. Luo, Z. Guo, *Macromolecules* **2011**, 44, 4382.
- [43] H. Li, M. A. Huneault, *Polymer* **2007**, 48, 6855.
- [44] T. Foresta, S. Piccarolo, G. Goldbeck-Wood, *Polymer* **2001**, 42, 1167.
- [45] R. Zannetti, G. Celotti, A. Fichera, R. Francesconi, *Die Makromolekulare Chemie* **1969**, 128, 137.
- [46] T. Foresta, S. Piccarolo, G. Goldbeck-Wood, *Polymer* **2001**, 42, 1167.
- [47] R. Thomann, C. Wang, J. Kressler, R. Mülhaupt, *Macromolecules* **1996**, 29, 8425.
- [48] S. H. Lee, E. Cho, S. H. Jeon, J. R. Youn, *Carbon* **2007**, 45, 2810.
- [49] S. H. Lee, M. W. Kim, S. H. Kim, J. R. Youn, *European polymer journal* **2008**, 44, 1620.
- [50] F. Du, R. C. Scogna, W. Zhou, S. Brand, J. E. Fischer, K. I. Winey, *Macromolecules* **2004**, 37, 9048.
- [51] P. M. Wood-Adams, J. M. Dealy, A. W. Degroot, O. D. Redwine, *Macromolecules* **2000**, 33, 7489.
- [52] A. Tuteja, P. M. Duxbury, M. E. Mackay, *Macromolecules* **2007**, 40, 9427.
- [53] J. Zhang, A. Panwar, D. Bello, T. Jozokos, J. A. Isaacs, C. Barry, J. Mead, *Environmental Science: Nano* **2016**, 3, 409.
- [54] A. Wadhawan, D. Garrett, J. M. Pérez, *Applied Physics Letters* **2003**, 83, 2683.
- [55] J. Walkiewicz, G. Kazonich, S. McGill, *Miner. Metall. Process* **1988**, 5, 39.
- [56] S. Frank, P. Poncharal, Z. Wang, W. A. de Heer, *Science* **1998**, 280, 1744.
- [57] Z. Ye, W. D. Deering, A. Krokhin, J. A. Roberts, *Physical Review B* **2006**, 74, 075425.
- [58] M.-K. Seo, J.-R. Lee, S.-J. Park, *Materials Science and Engineering: A* **2005**, 404, 79.
- [59] K. Wu, Y. Xue, W. Yang, S. Chai, F. Chen, Q. Fu, *Composites Science and Technology* **2016**, 130, 28.
- [60] X. Yan, J. Gu, G. Zheng, J. Guo, A. M. Galaska, J. Yu, M. A. Khan, L. Sun, D. P. Young, Q. Zhang, *Polymer* **2016**, 103, 315.

- [61] A. H. Alshehri, M. Jakubowska, M. Sloma, M. Horaczek, D. Rudka, C. Free, J. D. Carey, *Applied Physics Letters* **2011**, 99, 153109.
- [62] J. Stejskal, I. Sapurina, M. Trchová, J. Prokeš, I. Krivka, E. Tobolková, *Macromolecules* **1998**, 31, 2218.
- [63] Z. Guo, K. Shin, A. B. Karki, D. P. Young, R. B. Kaner, H. T. Hahn, *Journal of Nanoparticle Research* **2009**, 11, 1441.
- [64] M. Aggarwal, S. Khan, M. Husain, T. Ming, M. Tsai, T. Perng, Z. Khan, *The European Physical Journal B* **2007**, 60, 319.
- [65] S. J. Tans, A. R. Verschueren, C. Dekker, *Nature* **1998**, 393, 49.
- [66] J. Tauc, *Materials Research Bulletin* **1970**, 5, 721.
- [67] A. Hjelm, C. G. Granqvist, J. M. Wills, *Physical Review B* **1996**, 54, 2436.
- [68] N. Serpone, D. Lawless, R. Khairutdinov, *The Journal of Physical Chemistry* **1995**, 99, 16646.
- [69] M. B. Tzolov, T.-F. Kuo, D. A. Straus, A. Yin, Xu, *The Journal of Physical Chemistry C* **2007**, 111, 5800.
- [70] J. Wu, W. Walukiewicz, W. Shan, E. Bourret-Courchesne, J. Ager III, K. Yu, E. Haller, K. Kissell, S. M. Bachilo, R. B. Weisman, *Physical review letters* **2004**, 93, 017404.
- [71] O. Gülseren, T. Yildirim, S. Ciraci, Ç. Kılıç, *Physical Review B* **2002**, 65, 155410.
- [72] L. Yang, M. P. Anantram, J. Han, J. P. Lu, *Physical Review B* **1999**, 60, 13874.
- [73] Z. H. Ni, T. Yu, Y. H. Lu, Y. Y. Wang, Y. P. Feng, Z. X. Shen, *ACS Nano* **2008**, 2, 2301.
- [74] B. Hu, Y. Wu, *Nature materials* **2007**, 6, 985.
- [75] T. A. Skotheim, J. Reynolds, *"Handbook of Conducting Polymers"*, CRC press, 2007.
- [76] J. Guo, H. Gu, H. Wei, Q. Zhang, N. Haldolaarachchige, Y. Li, D. P. Young, S. Wei, Z. Guo, *The Journal of Physical Chemistry C* **2013**, 117, 10191.
- [77] T.-I. Su, C.-R. Wang, S.-T. Lin, R. Rosenbaum, *Physical Review B* **2002**, 66, 054438.
- [78] A. J. Hoffman, L. Alekseyev, S. S. Howard, K. J. Franz, D. Wasserman, V. A. Podolskiy, E. Narimanov, D. L. Sivco, C. Gmachl, *Nature materials* **2007**, 6, 946.
- [79] A. Sarkar, P. Ghosh, A. K. Meikap, S. K. Chattopadhyay, S. K. Chatterjee, M. Ghosh, *Solid State Communications* **2007**, 143, 358.
- [80] P. Bobbert, T. Nguyen, W. Wagemans, F. van Oost, B. Koopmans, M. Wohlgenannt, *Synthetic Metals* **2010**, 160, 223.
- [81] Y. Yosida, I. Oguro, *Journal of applied physics* **1999**, 86, 999.

Chapter 7. Conclusions and Future Work

Polymer nanocomposites (PNCs) consist of a polymeric material (e.g., thermoplastics, thermosets, or elastomers) and a reinforcing nanoscale material (nanoparticles). PNCs show major improvements in mechanical properties, UV-blocking properties, thermal stability, fire retardancy, and other areas. Overall, development of PNCs involves several key steps. Synthesis of size- and even shape-controlled nanoparticles is the first step for developing polymer nanostructured materials. Second is selection of the proper processing and fabrication methods to achieve nanodispersions of the nanoparticles in a selective polymer matrix. Third, characterization of nanoparticles is indispensable to understanding the behavior and properties of nanoparticles, striving to incorporate them into polymer systems in designing new nanomaterial systems with improved performance. Finally, the ultimate goal is to determine the performance of these polymer nanostructured materials using established test methods for specific applications. Moreover, there are many factors that influence the PNCs properties: (1) synthesis methods, such as melt compounding, solvent blending, *in-situ* polymerization, and emulsion polymerization; (2) the morphology of the PNCs; (3) types of nanoparticles and their surface treatments; (4) state of the polymer matrix, such as crystallinity, molecular weight, polymer chemistry, and whether thermoplastic or thermosetting. Thus, the interface between nanoparticles and the polymer matrix plays a very important role in determining the quality of the reinforcement of particles on the hosting polymers, as well as the diversity of the functions of PNCs. The magnetic PNCs with uniformly dispersed Fe_3O_4 NPs were systematically studied in Chapter 2. The magnetic properties, thermal stability, flammability properties and thermomechanical properties of the magnetic PNCs are improved with increasing NP loadings. However, the presence of the NPs restrains the large scale polymer chain movement, which easily causes the agglomeration of the NPs in the polymer matrix when the loading of the NPs reaches a high level. In chapter 3, the Au NPs are efficiently utilized as a discontinuous dispersion on the surface of the polymer. The real permittivity of the nanocomposite spheres is much higher than that of pure

PGMA spheres. An improved thermal stability is observed in the nanocomposite spheres. The calculated bandgap (0.91 eV) of the nanocomposite spheres is observed to be lower than that (4.92 eV) of pure PGMA spheres.

The solvent surface coating method is highly processable, which can achieve outstanding electrical conductivity with less CNTs compared with conventional methods. Thus the investigation of these progressive material systems can provide a guide for producing multifunctional polymer nanocomposites with controlled interface engineered nanostructures. Microwave radiation can be used for heating materials selectively. Highly electrically conductive PP/CNT PNCs were successfully synthesized by an efficient microwave solvent-free irradiation method under inert atmosphere and controlled treating time. This method gives a new perspective for designing CNT based conductive polymer materials on an industrial scale with environmentally friendly technology.

PNCs with interface engineered nanostructures can not only take full advantage of specific nanoparticles, but also can achieve designed nanostructures to satisfy or exceed especial functional requirements of PNCs. The control of interface engineered nanostructures of PNCs has a great potential to develop more high-performance multifunctional PNCs at an industrial scale. A possible research project for future investigation of PNCs with interface engineered nanostructures is that magnetic carbon nanoparticles can be prepared by the microwave energy-assisted pyrolysis, which could be introduced onto the surface of polymer granules by microwave radiation method to enhance the electromagnetic field absorbing property of PNCs. Other performance, such as thermal stability, magnetic, rheological, and flame-retardant properties, could also be investigated.

Vita

Xingru Yan was born in Xuzhou, China. She received her bachelor degree in Chemical Engineering and Technology from the Yangzhou University in 2011. After graduation, she joined Professor Zhanhu Guo's research group in Dan F. Smith Department of Chemical Engineering at Lamar University (LU) in August, 2011, and worked on new synthetic processes to prepare multifunctional nanocomposites and study special performances. Xingru obtained her Master of Science degree from the LU in December, 2012. After that, Xingru pursued doctoral education in Professor Guo's group continually and kept the same research areas. In January, 2015, Professor Guo joined the Department of Chemical and Biomolecular Engineering at University of Tennessee, Knoxville (UTK) as Associate Professor. Xingru continued her doctoral program at UTK and received a Doctor of Philosophy Degree in Chemical Engineering from the UTK in December, 2016.