	ト ツェ	
氏　　名	TU CE	
学位の種類	博士（工学）	
学位記番号	博第1102号	
学位授与の日付	平成29年9月6日	
学位授与の条件	学位規則第４条第１項該当　課程博士	
学位論文題目	Graphene Filled Polymer Nanocomposites: Morphology and Electrical Properties （グラフェン充填ポリマーナノコンポジット：モルホロジーと電気特性）	
論文審査委員	主 査	准教授　永田　謙二 教授　猪股　克弘 教授　樋口　真弘 教授　閻　寿科 （北京化工大学）

論文内容の要旨

1. Introduction

Conductive polymer nanocomposites (CPCs) consist of conductive fillers distributed throughout an insulating polymer matrix for the development of a conductive network. Because of their facile processing, flexibility, corrosion resistance, lightness, and cost effectiveness, CPCs can served as potential replacements for metals in many applications. Among various potential conductive fillers, graphene (a two-dimensional atomically thick sheet of sp^2-hybridized carbon atoms) has received considerable attention because of its superior mechanical strength, excellent thermal conductivity, and exceptional electrical properties. Specifically, the theoretical surface area of graphene is extremely high (estimated to be 2630 m^2/g), making it promising for the creation of a well-dispersed conductive network within the insulating polymer matrix. Such a network is expected to lead to a low electrical percolation threshold, which is indispensable for the development of high-performance CPCs as a high threshold is associated with (i) processing difficulties (a high melt viscosity), (ii) inferior ductility and toughness, and (iii) low economic feasibility.

2. Results

2.1. Morphology and Electrical Conductivity of PE/PP Blends Filled with TRG and SEG

CPCs were fabricated using melt compounding with polyethylene (PE) and polypropylene (PP) as

the polymer matrices. To investigate the effect of the graphene preparation method on the electrical properties of the nanocomposites, thermally reduced graphene oxide (TRG) and surfactant exfoliated graphene (SEG) were selected as conductive fillers. The TRG was better dispersed in the PE phase than the SEG; as a result, the TRG/PE/PP composites exhibited a lower electrical percolation threshold (3 wt.%) than the SEG/PE/PP composites (7 wt.%).

2.2. Influence of the Melt-Mixing Processing Sequence on the Electrical Conductivity of the PE/PP Nanocomposites Filled with TRG

The localization of TRG was tailored in the nanocomposites by varying the processing sequences of the TRG, PE, and PP components. Mixing the TRG/PP first and then melt-mixing the TRG/PP masterbatch with PE led to increased localization of TRG at the interface of the PE/PP blends. This structure was likely ideal for decreasing the percolation threshold, leading to a percolation threshold of less than 2 wt.%.

2.3. Effect of Graphene Localization on Electrical Conductive of SEG-Filled PE/PP Nanocomposites during Melt Blending

Morphology analysis using transmission electron microscopy (TEM) clearly revealed the importance of properly controlling the localization of SEG in the melt-mixed PE/PP nanocomposites. A low percolation threshold near 1 wt.% SEG was achieved when the localization of SEG at the PE/PP blend interface was optimized. In contrast, a percolation threshold of 7 wt.% was observed when the SEG localization was not optimized. Such procedures can indeed be expected to result in the localization of SEG at the PE/PP blend interface.

2.4. Dependence of Electrical Conductivity on Changing Phase Morphology for TRG Selectively Located at the Interface of PE/PP Nanocomposites

TRG was observed to be selectively dispersed in the PE phase of the TRG/PP/PE nanocomposites. However, localization of TRG at the interface of the PP/PE blends was observed for the (TRG/PP)/PE nanocomposites. For both the TRG/PP/PE and (TRG/PP)/PE nanocomposites, the formation of a co-continuous phase structure was the most effective approach for preparing electrically conductive nanocomposites. The electrical percolation threshold ranged from 0.5-1 wt.% for the (TRG/PP)/PE nanocomposites, which was much lower than that of the TRG/PP/PE nanocomposites (2 wt.%). For the (TRG/PP)/PE nanocomposites, as the TRG content exceeded the percolation threshold, the 2 wt.% TRG-filled nanocomposites exhibited a wide range of electrical capabilities for weight ratios of PP/PE varying from 10/90 to 80/20. This behavior was attributed to the interface-localized TRG connecting the dispersed TRG in the other phase, which facilitated the formation of a conductive graphene network throughout the nanocomposites.

2.5. TRG Filled PE/PP Nanocomposites Compatibilized by Ethylene-Butylene Copolymer and Their Electrical, Mechanical and Morphology Characterization

The elongation of the (TRG/PP)/PE nanocomposites increased from 3.86% to over 170% with the addition of ethylene-butylene copolymer (EBC). Moreover, an appropriate addition of EBC and a suitable mixing time greatly facilitated tuning of the electrical and mechanical properties of the (TRG/PP)/EBC/PE nanocomposites. Furthermore, the (TRG/PP)/EBC nanocomposites (non-PE nanocomposites) also exhibited extremely long elongation (over 270%) with an ideal dispersion of TRG in the PP phase, thereby leading to a very low percolation threshold of 0.5 wt.% (half that of the (TRG/PP)/PE nanocomposites) as well as a remarkable conductivity of 0.28 S/m.

2.6. Control of TRG at the Interfacial Region of the PE/PP Blends: Fabricated Conductive Nanocomposites with Ultralow Electrical Percolation Threshold

An ultralow electrical percolation threshold of 0.3 wt.% was achieved with the addition of ethylene–propylene copolymer (EPC). The EPC addition led to the preferential localization of TRG in the PE/PP blend interfacial region, which was attributed to the EPC improving the interfacial interactions with both the PE and PP phases. The addition of EPC also improved the mechanical properties of the neat PE/PP composites.

3. Conclusion

The effects of the type, phase morphology, dispersion, and localization of graphene as well as the addition of copolymers on the electrical, mechanical, and rheological properties of graphene-filled PE/PP nanocomposites were systematically investigated in this work. The structure consisting of graphene preferentially localized at the interface of the co-continuous phase morphology of PE/PP blends was optimal, resulting in an ultralow electrical percolation threshold of 0.3 wt.%.