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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 be 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 $2630 \text{ m}^2/\text{g}$), 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 Conductivity 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.%.

論文審査結果の要旨

本論文は、ナノカーボンであるグラフェンを導電性充填剤とし、2成分系より成るマトリックス高分子中に導入した導電性高分子複合材料の電気特性とモルホロジーの関係を、グラフェンの調製方法および複合材料の成形加工プロセスの両面から検討したものである。論文は以下の10章よりなる。

第1章は、序論であり、本研究の背景および本論文の目的、意義に関して述べている。

第2, 3章では、本研究で用いるグラフェンの調製方法に関し記述し、調製したグラフェンとマトリックス高分子（ポリエチレン/ポリプロピレン（PE/PP）ブレンド）との複合化方法と特性解析（キャラクタリゼーション）について述べている。

第4章では、膨張黒鉛から異なる調製方法で得られたグラフェンがPE/PP複合材料の電気特性とモルホロジーに及ぼす影響について検討をしている。熱的還元処理グラフェン（TRG）もしくは界面活性剤による剥離処理グラフェン（SEG）とPE/PPブレンドからなる複合材料の電気特性について、SEG/PE/PP複合材料のパーコレーション閾値が7wt%であるのに対し、TRG/PE/PP複合材料のパーコレーション閾値は約3wt%を示し、PE/PPブレンドが形成する相構造と複合材料中におけるグラフェンの分散性がグラフェンの調製方法にかなり依存することを明らかにした。

第5～7章では、第4章の知見をもとに、成形加工プロセス（混練条件）がTRGもしくはSEG充填PE/PP複合材料の電気特性とモルホロジーに及ぼす影響について述べている。複合材料中におけるグラフェンの分散状態、複合材料のモルホロジーと電気特性は、複合材料を構成する成分の混練プロセス（同時もしくは2段階）により著しく影響を受け、特に2段階混練プロセスを施すことでグラフェン（TRGもしくはSEG）をPE/PP界面に局在化でき、その結果、グラフェン充填複合材料のパーコレーション閾値を低減でき、導電性を向上できることを見出した。

第8, 9章では、第7章の知見をもとに、PEおよびPPと相溶化する共重合体を相溶化剤としてPE/PPブレンドに添加し、TRG/PE/PP複合材料におけるTRGの分散性と、TRG/PE/PP複合材料の電気特性と力学特性に及ぼす共重合体添加の影響について述べている。2段階混練プロセスと共重合体添加を組み合わせることで共重合体未添加系よりもTRGをPE/PP界面へ一段と局在化でき、その結果、TRG/PE/PP複合材料のパーコレーション閾値を低減でき、同時に力学特性も向上できることを明らかにした。

第10章は、総括であり、本研究で明らかとなった成果をまとめている。

以上のように、導電性充填剤であるグラフェンと相溶化剤である共重合体の種類と添加量及び、成形加工プロセスを制御することにより、複合材料中におけるグラフェンを局在化（特に、PE/PP界面領域へ選択的局在化）でき、グラフェンの低い充填濃度で複合材料の電気特性（導電性）の向上を可能とした。本論文は、複合材料の機能向上の新たな方法論を提示したものであり、その波及効果は大きい。本論文の成果は、学術雑誌3編の論文（すべて審査有）に掲載されており、学術的な価値を有すると判断される。したがって、本論文は博士（工学）の学位論文としてふさわしいものと認められる。