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論　　文　　題　　目	New Reactor Granule Technology for Fabrication of Functionally Advantageous Highly Filled Nanocomposites （機能性に優れた高添加コンポジット創生のための新規リアクターグラニュール技術の開発）
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論文の内容の要旨

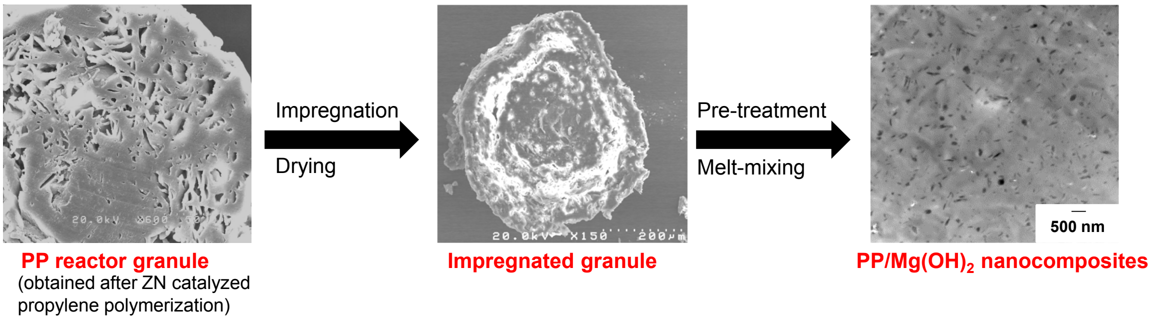
Background

Polymer nanocomposites are an emerging class of hybrid materials, where a small fraction of nano-sized filler offers enhancement in properties such as gas barrier, thermal stability, flame retardancy, mechanical properties and so on. A major issue associated with the fabrication of nanocomposites is the dispersion of nanofillers in the polymer matrix because of the great tendency of nanoparticles to agglomeration. Owing to the fact that nano-level dispersion is a prerequisite in realizing the performance of nanocomposites, various strategies such as addition of a compatibilizer or surface modifier have been employed. These dispersants improve the compatibility between the filler and the polymer, but at the same time result in unfavourable drawbacks such as additional cost, accelerated degradation, processability challenges and so on.

The dispersion problem is extremely challenging in the case of chemically inert polyolefins and also when a relatively high loading of nano-sized filler is required in specific applications such as flame retardancy, thermal conductivity and electrical properties [1-2]. Ideally, the best approach is to achieve nano-level dispersion without inclusion of any dispersants. Our research group has successfully disclosed a methodology for the fabrication of polyolefin nanocomposites based on an *in-situ* method *i.e. in-situ* formation of nanoparticles in the presence of the polyolefin. The novelty lies at the fact that it involves the impregnation of metal alkoxides in the porosity of polymer reactor granule and subsequent chemical conversion of the metal alkoxides into inorganic nanoparticles during melt-processing. The reported methodology is known as a new Reactor Granule Technology (RGT) and the concept was firstly exemplified by the preparation of polypropylene (PP)-based nanocomposites with TiO_2 for UV-cut transparent PP [3]. The *in-situ* fabrication of TiO_2 nanoparticles from impregnated titanium alkoxide and their extremely nice dispersion (at 3 wt%) proved the advantage of the new technology.

Aim

In this dissertation, I aimed at exploring and further developing the RGT for the fabrication of highly filled nanocomposites. Since it is difficult to control dispersion at high filler loading, in this research the challenge of controlling dispersion at high filler loading was targeted. RGT was developed for the fabrication of highly filled PP/$Mg(OH)_2$ nanocomposites to achieve flame retardancy (**Scheme 1**). Further, generalization of RGT to various kinds of highly filled nanocomposites was focused. Finally, I aimed at the development of highly thermally conductive polyolefin nanocomposites based on RGT.



Scheme 1. Concept of modified reactor granule technology

Experimental results and discussion

In ***Chapter 2***, the disclosed RGT was applied for the fabrication of flame retardant PP/$Mg(OH)_2$ nanocomposites. To achieve flame retardancy, a relatively high filler loading is required and a great challenge existed in controlling the dispersion at a high filler loading. A modified scheme including pre-treatment was invented and it was found that the hydrolysis of impregnated magnesium alkoxide prior to melt mixing enabled good dispersion of $Mg(OH)_2$ nanoparticles even at a high filler loading over 10 wt%. The flame retardant behavior of the nanocomposites was evaluated based on the limiting oxygen index (LOI) test. It was found that the prepared nanocomposites achieved a self-extinguishing level in flame retardation at 20-30 wt%, in comparison to 60 wt% for conventional PP/$Mg(OH)_2$ composites. The results revealed that the methodology not only offers uniform dispersion of nanoparticles in a dispersant-free manner, but also allows an access for the fabrication of highly filled nanocomposites (**Fig. 1**).

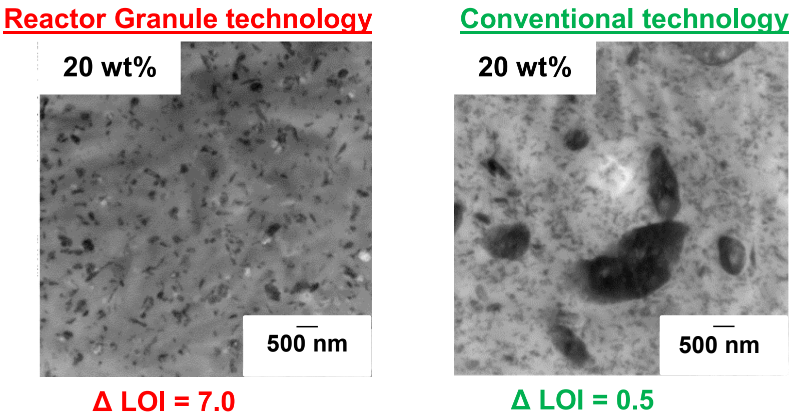


Fig. 1. Results for PP/$Mg(OH)_2$ nanocomposites.

To generalize the RGT to various kinds of highly filled nanocomposites, in ***Chapter 3***, the modified RGT was applied for fabrication of functionally advantageous PP nanocomposites with oxide nanoparticles, namely PP/TiO_2 and PP/Al_2O_3 nanocomposites. Firstly, the synthetic aspects of highly filled PP/TiO_2 and PP/Al_2O_3 nanocomposites were demonstrated. From SEM and EPMA analysis, it was proven that the porosity played an important role in effective confinement and pre-dispersion of the molecular precursors (**Fig. 2**). Furthermore, a hydrolytic pre-treatment was found to be crucial for the solidification of precursors in the porosity of PP reactor granule and for achieving excellent dispersion of nanoparticles at higher filler loading. Next, the advantages of reactor granule technology with focus on PP/Al_2O_3 nanocomposites were examined in terms of application-oriented properties. The excellent dispersion of Al_2O_3 nanoparticles led to significant improvement of mechanical properties of PP when compared to conventional composites. It was found that the dispersion state mainly affected the thermal conductivity of the resultant nanocomposites. At the filler loading of 5 vol%, the thermal conductivity of nanocomposites was almost double to that of neat PP (**Fig. 3**). From the research presented in ***Chapter 3***, it can be concluded that the RGT is a versatile approach for the fabrication of polyolefin-based nanocomposites, offering excellent dispersion over a wide range of filler loading and superior properties even without the use of any dispersants.

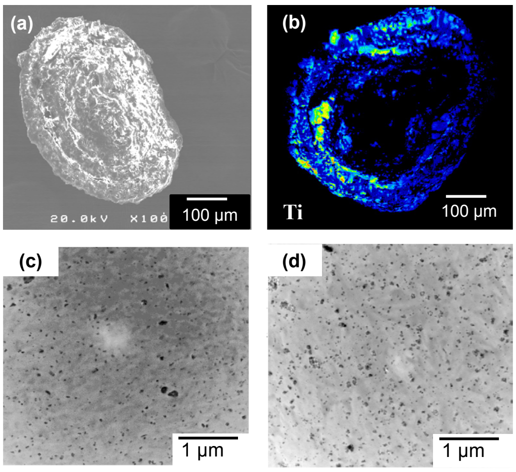


Fig. 2. (a,b) SEM and EPMA analysis of Ti(O*i*Pr)$_4$ impregnated reactor granule and (c,d) TEM micrographs of nanocomposites at 20 wt% filler loading.

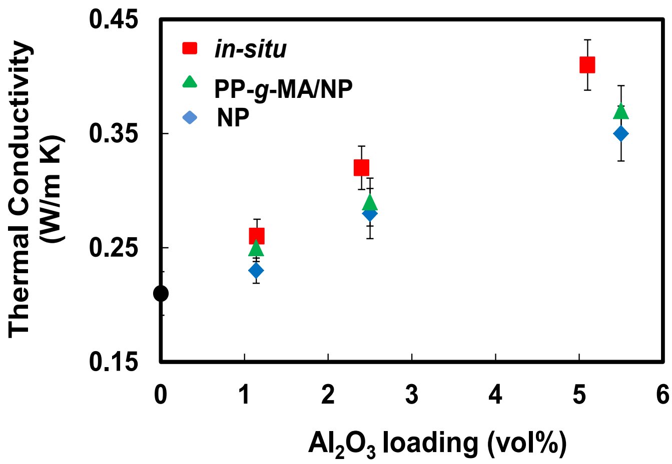
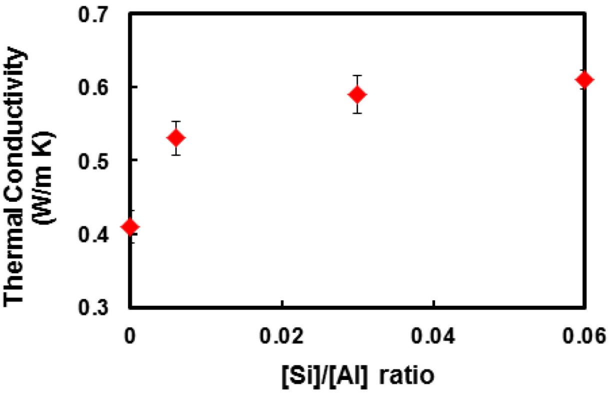


Fig. 3. Thermal conductivity of PP/Al_2O_3 nanocomposites.

In ***Chapter 4***, the development of heat releasing polyolefin nanocomposites based on RGT was targeted. Two different strategies were applied: i) the first one is based on the idea of forming filler-rich and polymer-rich domains in the resultant nanocomposites by diluting highly filled reactor granule with neat PP; and ii) employing a silane coupling agent as an interfacial modifier for *in-situ* generated Al_2O_3

nanoparticles. The effectiveness of the two employed strategies was studied based on the thermal diffusivity and conductivity of the resultant nanocomposites. It was found that the formation of filler-rich and -poor domains in the prepared nanocomposites resulted in the improvement of thermal conductivity. The usage of the silane coupling agent improved the thermal conductivity of resultant PP/Al_2O_3 nanocomposites, which was attributed to the improved interfacial interaction between Al_2O_3 nanoparticles and PP matrix (**Fig. 4**). From the research in ***Chapter 4***, it was found that the interfacial modification plays an important role in designing of thermally conductive nanocomposites.



Conclusion

From the research carried out in this thesis, it can be concluded that a novel and promising route for the fabrication of functionally advantageous highly filled polymer nanocomposites has been established in a simple and efficient manner. Furthermore, a few of the major challenges in the field of general polymer composites and hybrids such as a) use of dispersants to achieve nano-level dispersion, b) dispersion problem at high filler loading and c) problem in traditional compounding of thermoplastics in order to offer fabrication of a variety of value-added grades have been solved.

References

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Keywords: Polyolefins, Highly filled nanocomposites, Reactor granule technology, *In-situ* generation, Dispersant-free

論文審査の結果の要旨

本研究では、ポリオレフィン重合粉末への金属前駆体の含浸と溶融混練中の in-situ ナノ粒子合成から成るリアクターグラニュール技術に着目し、ナノ粒子を高充填率で高分散可能な新規ナ

ノコンポジット調製法を確立し、かつ、これを用いた種々の物性改良に成功した。

これまで化学的に不活性なポリオレフィンへの無機ナノ粒子の分散改良に関して、表面修飾や相溶化剤の添加、in-situ 重合法など様々な対策が提案されてきたが、5 ないしは 10 重量部を超える充填率でナノ粒子を高分散可能な技術は存在しなかった。本研究では、まず上述のリアクターグラニュール技術に改良を加え、ポリプロピレン中でマグネシウムエトキシドを水酸化マグネシウムに in-situ 化学変換する効率を飛躍的に改善する水蒸気処理によって従来の制限を突破し、30 重量部に及ぶ高充填率においても添加剤を一切加えることなく 100 nm 程度の水酸化マグネシウムナノ粒子が均一分散したナノコンポジット材料を得ることに成功した。また、得られたナノコンポジットが従来品と比較して結晶性・強度に優れること、従来品の半分の充填率（30 重量部）で自己消化性を示す難燃材料を与えることを見出した。このような改善は、高充填率かつ高分散という従来技術では成し得なかった材料設計の実現に尽きる。

続いて in-situ ナノ粒子合成の過程を解析し、金属前駆体の細孔充填と細孔中での固化が高充填率での高分散を実現する鍵因子であることを明らかにし、この知見に基づき開発技術を酸化チタンや酸化アルミニウムなどを含む酸化物系ナノコンポジットの調製へと拡張することに成功した。得られたナノコンポジット材料は、従来品と比較して幅広い充填率での分散性に優れ、特に高充填率において問題となる結晶性や力学強度の低下の問題を解決した。酸化アルミニウムは樹脂の熱伝導率改善に有用なフィラーであるが、本研究の技術は従来技術と比較してフィラー添加による熱伝導率の向上効率を 40%程度改善し、最終的に 20 重量部においてポリプロピレンの熱伝導率を 94%向上させた。

酸化アルミニウム系ナノコンポジットの熱伝導率改善が実用レベルに達する見込みが立ったことを受け、更なる技術改良を行い、ナノ粒子の濃度を偏在化させる技術、及び、マトリックスとナノ粒子の界面改質技術を提案した。特にアルミニウムアルコキシドとアルキルアルコキシシランを共含浸させ、その後酸化物へと in-situ 化学変換する技術は、アルキル基終端され界面接合性が大きく改善した酸化アルミニウムナノ粒子を与え、これによって熱伝導率の改善効率を 100%以上更新することに成功した。

以上、本論文は、疎水性樹脂にナノ粒子を高充填率で高分散させる世界初の技術を提供しており、有機／無機複合材料領域における学術的貢献は極めて大きい。よって博士（マテリアルサイエンス）の学位論文として十分価値あるものと認めた。