Title	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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New Reactor Granule Technology for the Fabrication of Functionally Advantageous Highly Filled Nanocomposites

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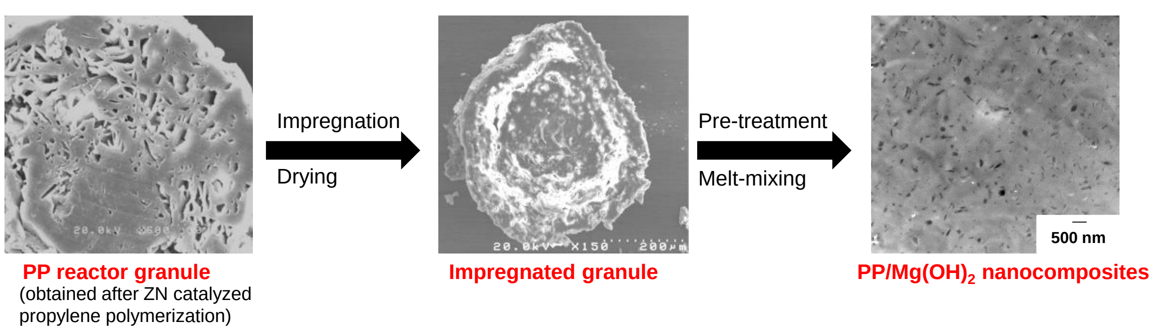
Background

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**).

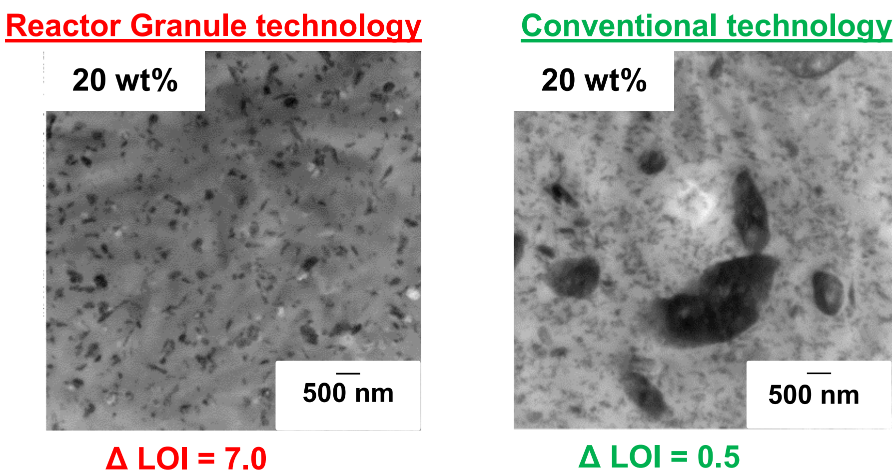
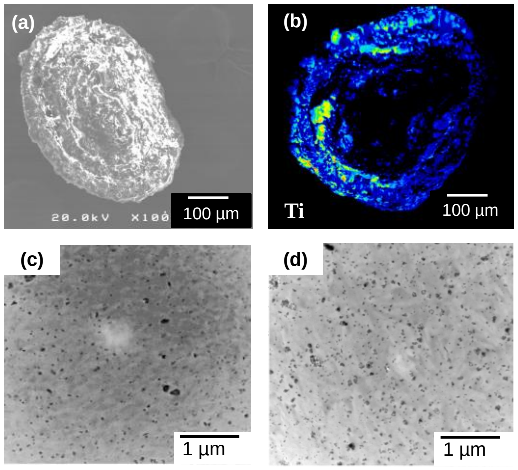


Fig. 1. Results for PP/$Mg(OH)_2$ nanocomposites.

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.



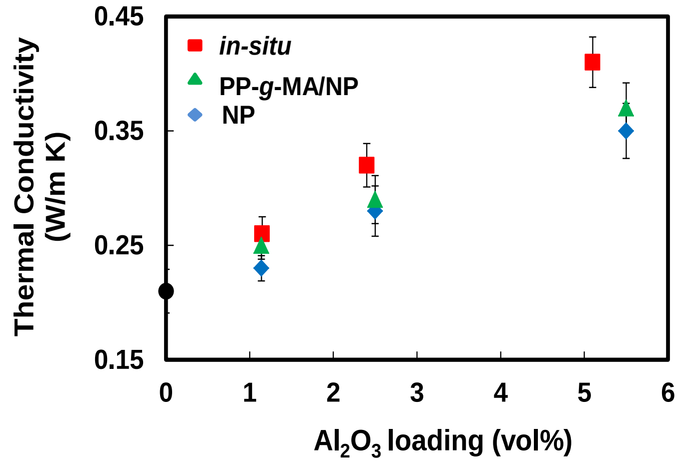


Fig. 2. (a,b) SEM and EPMA analysis of Ti(O*i*Pr)$_4$ impregnated reactor granule and (c,d) TEM micrographs of nanocomposites at 20 wt% filler loading.

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.

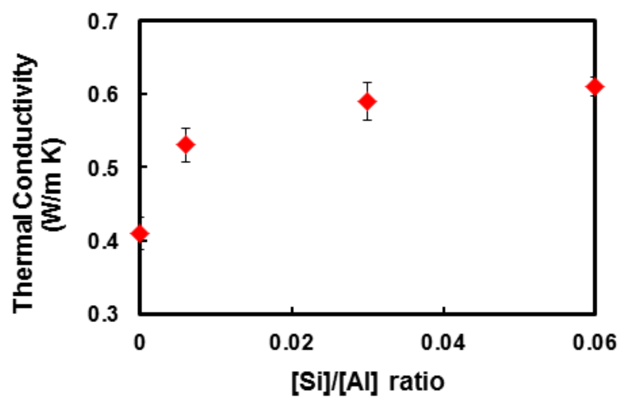


Fig. 4. Thermal conductivity of silane-modified *in-situ* PP/Al_2O_3 nanocomposites.

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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