Enhancement of polypropylene performance by adding a nucleating agent

Takahiro Inoue

Nucleating agents are important polymer additives that enhance the performance of crystalline polymers by promoting crystallization and controlling crystal structure. Among crystalline polymers, polypropylene (PP) utilizes many nucleating agents, such as talc, sorbitol derivatives, and metal salts of carboxylic acids. This study focused on calcium salts of 4-methyl cyclohexane-1,2-dicarboxylic acid (MHPA-Ca), a novel nucleating agent for PP to evaluate its nucleating performance for PP and the physical and optical properties of injection-molded products.

Firstly, the nucleating efficiency of MHPA-Ca was evaluated as compared with that of calcium salts of cyclohexane-1,2-dicarboxylic acid (HHPA-Ca), which has a similar structure to MHPA-Ca and is one of the most effective dispersed-type nucleating agents for PP, i.e., insoluble solid nucleating agents. The nucleating efficiency of dispersed-type nucleating agents is determined by the size and shape of solid particles. Therefore, both samples were prepared to have the same size and shape. The crystallization temperature (T_c), measured by differential scanning calorimetry (DSC), was used as an indicator to evaluate its nucleating efficiency. Non-isothermal crystallization measurements by DSC revealed that PP/MHPA-Ca exhibited a significantly high T_c compared to PP/HHPA-Ca and accelerated the crystallization rate. Consequently, the molecular orientation of PP/MHPA-Ca in injection-molded specimens increased, resulting in higher stiffness.

Secondly, the nucleating performance of MHPA-Ca was compared with that of 1,3:2,4-bis-*O*-(4-methylbenzylidene)-D-sorbitol (MDBS), which is known as a soluble-type nucleating agent, i.e., nucleating agents that dissolve in a molten polymer and segregated during cooling. PP/MHPA-Ca exhibited a pronounced nucleating performance even at a low addition level of 0.01 wt% and showed higher T_c over all additional ranges. This is due to differences in the mechanism of nucleating agents. While PP/MDBS showed comparable rigidity, it significantly improved transparency at additions of 0.2 wt% or more, whereas PP/MHPA-Ca showed only slight improvement. This indicates that transparency requires not only higher T_c but also the suppression of light scattering by the nucleating agent itself.

Finally, the shrinkage behavior of injection-molded products comprising PP with MHPA-Ca and MDBS was evaluated. These nucleating agents shortened the time until gate sealing at injection molding. Especially, PP/MDBS had a short gate-seal time compared with PP/MHPA-Ca. This indicated that MDBS exhibits excellent nucleating performance in a flow field. The shrinkage of PP with nucleating agents was prominent due to high crystallinity with rapid gate sealing. Furthermore, the shrinkage anisotropy of PP/MHPA-Ca was reduced compared with PP/MDBS at a low holding pressure. This is due to isotropic molecular orientation in the core region of injection-molded products of PP/MHPA-Ca. The structural characterization indicated isotropic molecular orientation in the core region of PP/MHPA-Ca. Crystal growth in all directions from numerous MHPA-Ca particles was responsible for the low level of molecular orientation in the core region. Considering that it is extremely difficult to achieve isotropic shrinkage for injection molded products of PP containing nucleating agents, this novel crystallization nucleating agent, MHPA-Ca, is industrially beneficial.

The conclusion of this doctoral thesis is as follows: This novel nucleating agent for PP, that is MHPA-Ca, showed superior nucleating performance compared with conventional nucleating agents. Furthermore, the shrinkage behavior of injection-molded products was isotropic compared with that containing conventional nucleating agents. These characteristics of the nucleating agents contribute to the enhanced performance of PP and make them suitable for industrial applications.

Keywords: polypropylene, nucleating agent, crystallization, injection molding, shrinkage