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Effect of polyhedral oligomeric silsesquioxane (POSS) reinforced polypropylene (PP) nanocomposite on the microstructure and isothermal crystallization kinetics of polyoxymethylene (POM)

Ali Durmus [a,*], Alper Kasgoz [a], Nevra Ercan [a], Dincer Akın [a], Selen Şanlı [b]

[a] Istanbul University, Engineering Faculty, Department of Chemical Engineering, Avcılar, 34320 Istanbul, Turkey
[b] EPSAN Plastics, R&D Department, Ali Osman Sönmez Cad. No:16, Bursa, Turkey

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ABSTRACT

In this study, effects of small amount of methyl-polyhedral oligomeric silsesquioxanes (methyl-POSS) on the microstructure and isothermal melt-crystallization behavior of polyoxymethylene (POM) were investigated, in detail. Introducing of methyl-POSS particles in POM phase was achieved via melt blending of methyl-POSS reinforced isotactic polypropylene (*i*-PP) nanocomposite as POSS carrier material with POM in a twin screw co-rotating extruder. Microstructural features of the POM/PP–POSS compounds were investigated with scanning electron microscopy (SEM) analysis. SEM analysis showed that the POM/PP–POSS compounds exhibited immiscible blend morphology. The POM, continuous matrix, phase includes a significant number of POSS particles due to interfacial interactions between the Si–O bonds of POSS and C–O bonds of POM, and resulted POSS migration from PP to POM phase during the melt processing. The kinetic parameters for the isothermal melt-crystallization process of the samples were determined with the Avrami and Lauritzen–Hoffman models. The crystallization activation energies were determined by the Arrhenius method. It was found that the PP–POSS nanocomposite significantly accelerated the isothermal crystallization rate of POM. Based on the results, it has been highlighted that POM compounds including a small amount of PP–POSS nanocomposite as POSS carrier material can be successfully used in the production of injection molded POM parts because the POM/PP–POSS compounds yield much faster molding cycle thus production rate than the POM.

1. Introduction

Polyoxymethylene (POM) or polyacetal is one the most widely used engineering thermoplastics in many application areas such as automotive industry and parts in mechanical and electromechanical equipments etc. due to its superior physical properties. POM exhibits higher crystallinity than other semi-crystalline polymers, high tensile and flexural modulus, excellent dimensional stability and wear and friction properties [1]. On the other hand, POM is weak for thermal degradation, weathering and environmental conditions since the methyl oxide bonds ($-CH_2-O-$) in the structure are easy to break under heat and oxygen [2].

It is well known that physical properties of a semi-crystalline polymer are governed by the supramolecular structure, which in turn is controlled by the crystallization. Crystallization behavior of POM compounds and composites depends on the compositional and microstructural parameters such as physical properties of the second phase and/or fillers like surface character, loading amount, geometry, dispersion etc. and processing conditions rather than the structural features of matrix because POM homo or copolymer exhibits a quite simple chain structure and relatively higher crystallization rate compared to other industrial thermoplastics.

POM compounds are prepared with conventional melt processing methods and end-products are generally used as injection molded parts in many applications. Therefore, comprehensively understanding of melt-crystallization of POM compounds provides important knowledge for managing of injection molding operations in plastic industry and the physical properties of products. Many studies have been reported on the nucleation effects of inorganic fillers such as glass fiber [3,4], various types of minerals, silica, alumina, titanium dioxide (TiO_2) and nanoparticles [5–12] and organic additives [13–15] on the crystallization kinetics of semi-crystalline thermoplastics. On the other hand, crystallization

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* Corresponding author. Tel.: +90 212 591 24 80; fax: +90 212 473 70 38.
E-mail address: durmus@istanbul.edu.tr (A. Durmus).

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kinetics of semi-crystalline polymer blends have also been studied [16–19]. Hu and Ye investigated isothermal and non-isothermal crystallization behavior and morphology of POM blended with small amount of polyamide (PA) (0.2–0.6 wt%) [20]. They demonstrated that the addition of PA reduced the spherulite size and improved the crystallization growth rate and the degree of crystallinity of POM due to the nucleation effect of PA as the high-molecular nucleus. Masirek and Piorkowska found that the addition of small amount of submicron poly(tetrafluoro ethylene) (PTFE) particles (0.005–0.5 wt%) enhanced the nucleation of isotactic polypropylene (*i*-PP) and POM crystallization [21]. They also declared that the PTFE particles improved the elastic modulus of *i*-PP and POM. Ding et al. studied the effect of polyvinylidene fluoride (PVDF) on the crystallization behavior of POM [22]. They pointed out that addition of PVDF greatly decreased the spherulitic size of POM, but the structure of hexagonal POM crystal was not changed. Furthermore, they also reported that the dispersed PVDF acted as heterogeneous nuclei and accelerated the rate of nucleation, but hindered the crystal growth rate of POM. One of the interesting studies on the crystallization behavior of POM in a multi-component system was the study by Goossens and Groeninckx [23]. They investigated the influence of the curing process of diglycidyl ether of bisphenol A (DGEBA) based epoxy resin and the resulting reaction-induced phase separation (RIPS) on the crystallization and melting behavior of polyoxymethylene (POM) in the POM/epoxy blends. They found that the isothermally crystallized POM was dramatically influenced by the conversion degree of the epoxy resin and more perfect crystals were formed if the epoxy resin could polymerize during the crystallization process.

Few papers have also been published about the effects of different fillers and/or organic and inorganic nucleating agents on the crystallization of POM [24–27]. Xu and He investigated the crystallization kinetics of POM including attapulgite and diatomite as low-cost inorganic nucleating agents [26,27].

Polyhedral oligomeric silsesquioxane (POSS) molecule is a rigid, three dimensional, cage-like silicon-oxygen nanostructured skeleton with a general formula of $R(\mathrm{SiO}_{1.5})_n$ where R is hydrogen or an organic group (aliphatic or aromatic or any of their derivatives) and $n = 8$, 10 or 12. Specific geometry and size of POSS molecules (1.5–3 nm), its chemical versatility for grafting of various types of functional groups and commercial availability of intermediates or many different varieties has attracted great technical attention for application of POSS reinforced and/or modified polymers. Dispersion of POSS nanoparticles in a polymer phase provides many structural and physical advantageous such as higher mechanical properties, thermal and oxidative stability, easy crystallization and higher crystallization rate, molecular sieving and selectivity in gas separation and pervaporation membranes etc [28–30]. Effects of various types of POSS molecules on the microstructure, crystallization behavior and physical properties of semi-crystalline thermoplastics have been studied in recent years [31–37]. To the best of our knowledge, only two papers published on the microstructure and thermo-mechanical properties of POSS-reinforced POM [38,39]. Illescas et al. investigated the morphology and thermo-mechanical behavior of POM composites filled with monosilanolisobutyl polyhedral oligomeric silsesquioxane (msib-POSS) prepared with direct melt blending at loadings between 0 and 10 wt% of msib-POSS [39]. They reported that formation of hydrogen bonding interactions between the POM and Si–OH groups of msib-POSS increased their mutual compatibility and lead to nanometer-size dispersion of some msib-POSS molecules. They also found that such interactions did not prevent aggregation of POSS during melt blending, but lead to micron-scale msib-POSS domains.

In this study, effects of small amount of methyl-polyhedral oligomeric silsesquioxanes (methyl-POSS) on the microstructure and isothermal melt-crystallization behavior of polyoxymethylene (POM) were investigated, in detail. Introducing of methyl-POSS into the POM phase was achieved via a different compounding route from the conventional direct blending method, for the first time. Methyl-POSS reinforced polypropylene (*i*-PP) nanocomposite was used as POSS carrier material or masterbatch. Hence, introducing of POSS molecules into the POM phase was carried out via blending of two granulated polymers (POM and PP/POSS nanocomposite) by a simple melt processing method.

2. Experimental

2.1. Materials

Polyoxymethylene (POM) used in this study is a commercial polyacetal copolymer, Kepital® F20, with the molecular formula of $[\mathrm{CH_2-O}]_n - [\mathrm{CH_2{-}CH_2-O}]_m$, the density of 1.41 g cm^{-3} (ASTM D792) and MFI of 9.0 g 10 min^{-1} (under the condition of 10 kg, 220 °C). PP–POSS nanocomposite is also a commercial grade material purchased from Aldrich, product number of 565628. It is an isotactic polypropylene (*i*-PP) based nanocomposite reinforced with 10 wt% of methyl-polyhedral oligomeric silsesquioxanes (methyl-POSS).

2.2. Sample preparation

Samples were prepared by melt processing in a lab-scale twin screw extruder (Rondol Micro Lab., UK, D:10 mm, L/D: 20) with a screw speed of 50 rpm. Screws of the extruder were configured as including 3D of 4 × 60° followed by 2D of 4 × 90° kneading segments. A temperature profile of 110–160–180–180–180 °C was applied throughout the barrel from the feeding zone to die. A rod die was used for the preparing of granulated sample for the DSC and SEM studies. Before the melt processing, all materials were dried in a vacuum oven overnight at 70 °C. The POM, *i*-PP and PP–POSS nanocomposite were also processed at the same conditions. Sample compositions are listed in Table 1. Sample notation of PP-10 and PP-20 indicate the POM/PP–POSS compounds including 10 and 20 wt% of PP–POSS nanocomposite which correspond to nano-POSS amount of 1 and 2 wt% in the composition, respectively.

2.3. Microstructure and morphology studies by SEM

Morphological and microstructural features of the PP–POSS nanocomposite and POM/PP–POSS samples were investigated by a field emission scanning electron microscope (FE-SEM, FEI-Quanta FEG 450). Cryo-fractured cross-sections of the extrudate samples were directly imaged in the electron microscope after a proper sample preparation of sputter-coated with gold. The methyl-POSS particles in the PP–POSS nanocomposite were also characterized by the energy dispersive X-ray spectroscopy (EDS) analysis on the sample images.

Table 1
Sample compositions.

Samples	wt%		
	POM	PP–POSS	POSS
POM	100		
PP-10	90	10	1.0
PP-20	80	20	2.0
PP–POSS		100	10.0