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Thermal and mechanical properties of polyhedral oligomeric silsesquioxane (POSS)/polycarbonate composites

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Abstract

A series of composite materials were produced incorporating polyhedral oligomeric silsesquioxane (POSS) derivatives into polycarbonate (PC), by melt blending. Significant differences in compatibility were observed depending on the nano-scale filler's specific structure: trisilanol POSS molecules generally provided better compatibility with PC than fully-saturated cage structures, and phenyl-substituted POSS grades were shown to be more compatible with PC than fillers with other functional groups. Trisilanolphenyl-POSS/PC composites possess the best overall performance among the POSS materials tested. The high compatibility between the trisilanolphenyl-POSS and polycarbonate matrix results in generation of transparent samples up to 5 wt% POSS content. Slightly enhanced mechanical properties including tensile and dynamic mechanical modulus are observed with the increase of trisilanolphenyl-POSS loading at the cost of decreasing ductility of the nanocomposites. Importantly, upon orientation of the PC/POSS nanocomposite, crystallization of POSS within the oriented material results—this observation is consistent with a growing number of observations which suggest that 'bottom-up' formation of structures incorporating multiple POSS cages result from orientation of these nanocomposites, and that the hybrid organic–inorganic inclusions may be at the heart of observed nano-scale reinforcement.

Keywords: Nanocomposite; Blend; Polycarbonate

1. Introduction

Polyhedral oligomeric silsesquioxane (POSS™) molecules possess a cage-like structure (1–3 nm in size) and a hybrid chemical composition ($RSiO_{1.5}$) which is intermediate between silica (SiO_2) and silicones (R_2SiO) [1]. Their well defined structure contains a stable inorganic Si–O core surrounded by substituents which can be modified to present a wide range of polarities and reactivities. POSS molecules can be incorporated into polymer systems through blending [2], grafting or copolymerization [3–9] aiming at nanostructured polymeric materials whose properties bridge the property space between organic plastics and ceramics.

Recent studies on POSS-containing hybrid copolymers and thermosets have been reported indicating reinforced mechanical [6–8] and thermal properties [7,9]. The present study focuses on the thermal and mechanical properties of blends of POSS derivatives and polycarbonate (PC). Here POSS is expected to act as a nano-scale filler to modify the polycarbonate matrix and potentially result in nanocomposites with new or improved properties. Compared with traditional fillers, POSS is known in some cases to exhibit enhanced compatibility resulting from a match between its organic substituents and the matrix polymer. In this manner, control of the microstructure of the POSS nanocomposites can be achieved and is key to the performance and properties of such materials [3,9]. It is generally believed that nanoscale POSS domains with ordered and self-assembled features in a polymer matrix are highly desirable and lead to the observed improvement in material properties [10–13].

The current work focuses on the compatibility of different five different POSS structures (Scheme 1) with a polycarbonate matrix and the effect of POSS concentration on the thermal and mechanical properties of POSS/PC nanocomposites. Differences between composites containing fully-condensed POSS cages, and those possessing a hybrid inorganic–organic 3D partial cage-like structure bearing three silanol (Si–OH) groups (Scheme 1(b)) will be examined. It was recently reported that the trisilanol POSS grades, especially isooctyl trisilanol POSS, exhibit better compatibility with PET, as judged by single phase melts and optically transparent extrudate [14].

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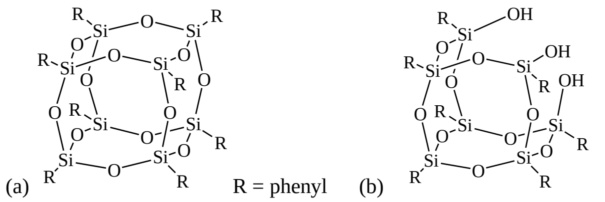


Scheme 1. Typical chemical structures of POSS molecules: (a) octaphenyl-POSS (MS0840); (b) trisilanolphenyl-POSS (SO1458) when R = phenyl, and trisilanolisooctyl-POSS (SO1455) when R = *i*-octyl.

Additionally, the properties of a blend of trisilanolphenyl-POSS with a polycarbonate/polysulfone polymer blend (HTLT Z-1050) was briefly investigated in this study.

2. Experimental section

2.1. Materials

Dow CALIBRE® 200-14 and BASF Makrolon 2405 Polycarbonate grades were used as received. POSS derivatives were supplied by Hybrid Plastics, Inc. and used as received. A polycarbonate–polysulfone thermoplastic polymer blend (HTLT Z-1050) was supplied by Suncolor Co. and used as received. Prior to compounding the polymer pellets were dried for at least 6 h under vacuum at 100 °C.

2.2. POSS/PC sample preparation

Polycarbonate was blended with different levels of POSS using a DACA model 20000 twin-screw co-rotating micro-compounding extruder (13.75 mm screw diameter/108 mm length). The blending was carried out at 290 °C and a screw speed of 100 rpm for 5 min prior to extrusion. During the extrusion process, the extruded samples were visually inspected for qualitative transparency. The samples were then compression molded into films (not constrained inside of a mold) for mechanical testing using a Carver model C press. The PC composites were first heated at 280 °C for 3–4 min and a rapid compression (5–6 ton), followed by release of pressure to remove any trapped gas bubbles. The samples were then molded at 280 °C under 6–7 ton pressure for 3–4 min and cooled rapidly between two water-chilled aluminum plates. The PC composite films (0.2–0.3 mm thickness) were obtained and evaluated for transparency. For the trisilanolphenyl-POSS/HTLT Z-1050 composite, the compounding was performed at 320 °C and 100 rpm screw speed/4 min prior to extrusion, and the compression molding was carried out under 6–7 ton pressure for 3–4 min at 310 °C.

2.3. Differential scanning calorimetry (DSC)

The thermal behaviors of the POSS/PC composites were measured using a TA Instruments DSC 2910 equipped with a pressure DSC Cell. Samples (4–8 mg) were tested at a heating rate of 10 °C/min and results from the second heating are reported. Thermal data analysis was performed using TA Instruments Universal Analysis Software.

2.4. Dynamic mechanical analysis

A Tritec 2000 DMA (Triton Technology Co.) was used in tensile mode at an oscillatory frequency of 1 Hz with applied 1% strain for all samples. The temperature scan was performed at 3 °C/min heating rate in the range from room temperature to around 180 °C for PC composites and 280 °C for HTLE Z-1050 composite. Sample dimensions were typically 4.9 mm long, 9.8 mm wide and 0.2–0.3 mm thick.

2.5. Tensile testing

Sample films were die cut into standard ASTM D 638V dog bone shaped test specimens with the geometry shown in Scheme 2. The microtensile tests were carried out on an Instron model 5565 at an extension rate of 2 mm/min at room temperature (~23 °C). Five specimens of each composite were tested and then averaged results and standard deviations were reported.

2.6. Thermal gravimetric analysis (TGA)

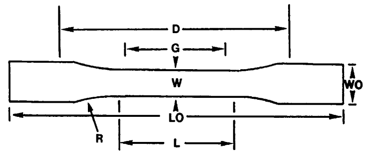
The thermal stability of the samples was measured by thermogravimetric analysis using a TA Instruments 2950 High Resolution Thermogravimetric Analyzer. Sample sizes ranged from 5 to 15 mg. Weight loss was traced as samples were heated at a rate of 10 °C/min from room temperature to 900 °C under a dry nitrogen purge of 90 ml/min.

2.7. Wide-angle X-ray diffraction (XRD)

The XRD measurements were carried out at room temperature on a Rigaku X-ray diffractometer in normal reflection mode with Ni-filtered Cu Kα radiation ($\lambda = 1.54$ Å). After the sample was loaded, the alignment procedure was followed to ensure the accuracy of the θ angle. For oriented samples, the sample specimens were rotated to obtain the diffraction profiles at parallel and perpendicular directions.

2.8. Izod impact tests

Two grades of PC, Bayer Makrolon 2405 and Dow Calibre 200-14, as well as two nanocomposites, PC/3 wt% PM 1271



D = 25 mm G = 10 mm
W = 3.2 mm LO = 63 mm
L = 10 mm WO = 10 mm
R = 5.0 mm

Scheme 2. The test specimen for tensile measurement. $D = 25$ mm; $G = 10$ mm; $W = 3.2$ mm; LO = 63 mm; $L = 10$ mm; WO = 10 mm; $R = 5.0$ mm.