34.1 DEFINITION, HISTORY AND SYNTHESIS

The Polyhedral Oligomeric Silsesquioxanes (POSS) are an interesting class of three-dimensional inorganic/organic hybrids with the generic formula of (RSiO$_3$)$_2$, as shown in Fig. 34.1 [1–4]. These molecules contain an inner inorganic framework covered by inert and/or reactive organic substituents. POSS molecules with well-defined shapes and sizes ranging from 1–3 nm have been described as the smallest version of colloidal silica. The R’s can be inert organic groups used to enhance miscibility with polymeric host materials [5,6]. Making one or more of the R groups reactive permits bonding of the cages to polymers by copolymerization [7] or grafting [8] onto backbone chain. Incorporating such POSS cages into polymeric materials has already provided useful property enhancements, such as increased glass transition temperature, decomposition temperature, and mechanical strength. Because of the tailorability of POSS molecules, they can also be designed to probe the molecular basis of reinforcement, and to establish structure–property relationships that can then be exploited to optimize properties for particular applications. These POSS reagents have a number of desirable physical properties. For example, they are soluble in common organic solvents such as tetrahydrofuran (THF), toluene, chloroform, and hexane [9,10].

POSS was discovered in 1946 by Scott [11]. After 1990 the field developed rapidly due to the work of two groups: the Feher group at the University of California-Irvine and the Lichtenhan group at the Air Force Research Laboratory. The Feher group devised many methods for synthesizing and chemically modifying structurally well-defined Si/O frameworks [3,4,12–29]. The Lichtenhan group, on the other hand, pioneered the use of discrete POSS in polymer-related applications [7,9,30–32].

The synthesis of fully condensed POSS frameworks starts with the controlled hydrolysis and condensation of trifunctional organosilicon monomers (i.e., RSiX$_3$, R = c-C$_6$H$_{11}$, Cy or c-C$_5$H$_9$, Cp) [13,16,33]. The functionalization of the POSS framework is then easily accomplished by corner capping of the POSS-trisilanols with silane coupling agents containing organic groups suitable for polymerization [1,13,16]. This methodology provides access to a family of cycloalkyl-substituted POSS monomers, each containing one polymerizable group, as shown in Fig. 34.2 [1]. In cases where the appropriate functionality is not directly available by the corner capping sequence, subsequent functional group transformation of the reactive group on a unique silicon atom is possible [1]. Multifunctional POSS derivatives can be made by the condensation of R’Si(OEt)$_3$, as described above, where R’ is a reactive group [2,34]. Another approach involves functionalizing POSS cages that have been formed [35–37].

The detailed methods of POSS synthesis have been reviewed by Voronkov et al. in 1982 [2] and Feher and co-workers in 2000 [28]. It is now possible to prepare a range of useful Si/O frameworks from relatively inexpensive feedstocks. A variety of POSS reagents with one or more covalently bonded reactive functionalities has become commercially available from the Hybrid Plastics Company (http://www.hybridplastics.com).

34.2 NANOREINFORCED POSS-BASED POLYMER AND COPOLYMERS

Because of its chemical nature, POSS is easily incorporated into common plastics via copolymerization or blending, requiring little or no alteration to existing manufacturing processes. Incorporation of POSS reagents into
linear thermoplastics or thermoset networks can be used to modify composition, local structure, and chain mobility. These modifications can ultimately affect the thermal, oxidative, and dimensional stability of many polymeric resins, resulting in improvements in properties, including increased glass-transition temperature, decomposition temperature and modulus, reduced flammability, and increased gas permeability. Depending on the number of POSS functional groups, different architectures of POSS/polymer composite can be obtained, as shown in Fig. 34.3.

A variety of POSS-containing polymer and copolymers have been synthesized based on radical [7], conventional [7,30], and atom-transfer [38], condensation [9,39] and ring-opening metathesis polymerization (ROMP) [40,41] techniques. Copolymers obtained in this manner with POSS units attached as dangling blocks to the polymer backbone include copolymers of polysiloxane [9,42], poly(methyl methacrylate) [30,32,38], poly(4-methylstyrene) [7,43–45], epoxy [39,46], polynorbornene [47–49], and polyurethane [50,51], et al. Monofunctional and difunctional POSS is commonly used in this case. The resulting materials represent a new category of polymers characterized by the presence of bulky POSS nanoparticles. There are some very useful review papers available on this subject [52,53].

Here, we will use POSS-styrene system as paradigm to explain the synthesis and properties of POSS-containing polymers and copolymers. Other systems are listed in Table 34.1, along with references. POSS-styrene polymers and copolymers with 4-methylstyrene have been extensively studied by Haddad et al. [7,44]. The reaction scheme is shown in Fig. 34.4.

The glass transition temperature $T_g$ of poly(co-POSS-4-methylstyrene) varies linearly with mole percent POSS in the copolymer, from 116 °C for pure poly(4-methylstyrene) to approximately 400 °C for pure polyPOSS-substituted styrene. The decomposition temperature of the styril backbone dramatically increases, presumably because the large pendant POSS groups reduce chain mobility. POSS modification also effects dynamical mechanical properties [43]. By varying the R groups on the POSS cages, the DMTA spectra show an increase in tan $\delta$ with $R = Cy>Cp$ (Cy:cyclohexyl, Cp:cyclopentyl) and a plasticization effect when $R = i-$Bu. This result supports the conclusion that R groups on the POSS cages result in significant changes of bulk mechanical properties [48]. Coughlin et al. are studying hemi-telechelic POSS-polystyrene and are investigating

![Figure 34.1. Schematic structure of POSS(R = c-C6H11(Cy), c-C5H9(Cp); X = reactive group).](image)

![Figure 34.2. Some of the functionalities that can be prepared from POSS-trisilanol precursors [1].](image)