REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)* 29-11-2011	**2. REPORT TYPE** Conference Paper	**3. DATES COVERED** *(From - To)*

4. TITLE AND SUBTITLE

Silicon-Containing Polymers and Composites

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

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5d. PROJECT NUMBER

5f. WORK UNIT NUMBER
23030521

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

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8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

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10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S NUMBER(S)
AFRL-RZ-ED-TP-2011-555

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited (PA #111049).

13. SUPPLEMENTARY NOTES
For presentation at the American Chemical Society National Conference, San Diego, CA 25-29 Mar 2012.

14. ABSTRACT

There are many examples of improved oxidation-resistance in organic polymeric materials achieved through the incorporation of silicon-containing compounds. These compounds are often organically-modified particles, such as silicas, silicates, clays, or polyhedral oligomeric silsesquioxanes, which can be mechanically blended into a wide variety of polymer matrices. However, in order to achieve improved dispersion of the silicon phase, it is often desirable for the silicon-containing compound to be covalently bound to the polymer backbone. This can be accomplished by polymerization of silicon-containing monomers, copolymerization of silicon monomers with desired organic monomers, or chemical modification of organic polymers by reactive silicon-containing molecules. In thermoplastic polymers, examples of both blended and covalent incorporation are common. In thermosets, however, the covalent approach is typically desired due to the ease of monomer processing and the low potential for phase separation during cure. A variety of silicon-containing fillers monomers, polymers, and composites will be discussed, as well as the advantages of each.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON** Dr. Joseph M. Mabry
a. REPORT **Unclassified**	**b. ABSTRACT** **Unclassified**	**c. THIS PAGE** **Unclassified**	SAR	4	**19b. TELEPHONE NUMBER** *(include area code)* N/A

Silicon-Containing Polymers and Composites

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Silicon-containing polymers and composites

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Introduction

Polymeric materials are typically tough, lightweight, and easy to process. However, they often lack resistance to oxidation and degrade at high temperatures. On the contrary, ceramic materials are usually thermally stable and resistant to oxidation. However, they are often brittle and difficult to process. The subject compounds contain silicon in their structure, and are often surrounded by organic functionality, which either improves polymer miscibility, or adds desired functionality. Because of the wide-range of commercially-available polymers and resins, several of these silicon-containing compounds have been incorporated into thermoplastic and/or thermosetting polymer systems and found to improve various polymer properties.

There are many examples of improved oxidation-resistance in organic polymeric materials achieved through the incorporation of silicon-containing compounds. These compounds are often organically-modified particles, such as silicas, clays, and silsesquioxanes, which can be mechanically blended into a wide variety of polymer matrices. However, in order to achieve improved dispersion of the silicon phase, it is often desirable for the silicon-containing compound to be covalently bound to the polymer backbone. This can be accomplished by polymerization of silicon-containing monomers, copolymerization of silicon monomers with desired organic monomers, or chemical modification of organic polymers by reactive silicon-containing molecules. In thermoplastic polymers, examples of both blended and covalent incorporation are common. In thermosets, however, the covalent approach is typically desired due to the ease of monomer processing and the low potential for phase separation during cure.

A variety of silicon-containing nanoparticles are currently commercially available, including layered and linear silicates (clays), nano-silicas, and Polyhedral Oligomeric Silsesquioxanes (POSS).[1-3] These are either inorganic or inorganic/organic hybrid materials, which are commonly used for the improvement of polymer properties. In addition to these more common, nano-sized, Si-containing polymer fillers, others can be readily produced in the laboratory.

Polymers and resins are often reinforced with high-surface area, nano-scale inorganic materials to produce polymer nanocomposites.[3,4] In order to optimize miscibility and property enhancement, the polar inorganic materials must be compatible with the usually non-polar polymers. This is often achieved by organic functionalization of the inorganic component. One example is the trimethylsilylation of silica by treatment with hexamethyldisilazane or other silylating agents, which converts many of the polar silanol groups into non-polar trimethylsiloxy groups.[5-7]

Polyhedral Oligomeric SilSesquioxanes (POSS), layered and linear silicates (clays), and nano-silicas are nanoscale materials used for the property enhancement of commercial polymers and composite resins. These inorganic materials are often surrounded by organic functional groups, which can be utilized for polymer and resin compatibility, as well as to add desired composite functionality. In fact, the alkyl or aryl groups surrounding the silicate core can be chosen to match the polymer matrix in order to fine-tune desired miscibility characteristics. The resulting organic/inorganic hybrid nanocomposite materials are being examined for use in many commercial and military applications.[8-11] For example, thermo-mechanical properties have been improved in space-survivable coatings and fire-resistant materials.[1, 8-11]

The inorganic core in POSS molecules is a cage structure consisting of eight silicon and twelve oxygen atoms. Each tetravalent silicon atom is attached to three oxygen atoms, leaving a single site of valency for bonding with an organic group. Therefore, POSS are defined as silsesquioxanes. Due to their physical size, POSS incorporation in polymers generally serves to reduce chain mobility, thus affecting both thermal and mechanical properties.[1,10-11]

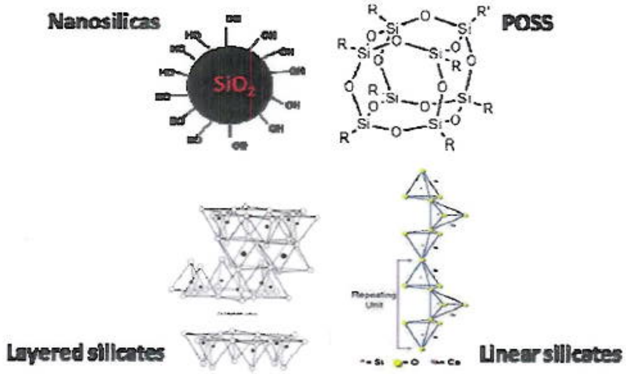

Figure 1. Generic structures of nanosilicas, Polyhedral Oligomeric Silsesquioxanes (POSS), and layered- & linear-silicates (clays).

In the structure of typical clay compounds, each silicon atom is surrounded by four oxygen atoms, leaving no valency for bonding with an organic group. Therefore, they are defined as silicates. However, clays often contain metal cations, which can undergo ion exchange reactions, allowing the addition of organic cations, which can be utilized for polymer compatibility. Due to their structure, clay-filled polymers generally exhibit improved thermal and mechanical properties, compared to the unfilled polymers and resins.

Fumed-silicas possess an amorphous core consisting of silicon and oxygen atoms. Each tetravalent silicon atom is attached to four oxygen atoms, leaving no additional valency. Therefore, fumed-silicas are also silicates. However, most silicas also contain hydroxyl groups, typically on the particle surface. These silanol groups allow organic modification, such as the trimethylsilylation mentioned previously.[5-7] Largely due to their size, nano-silicas can also reduce chain mobility and affect polymer properties.

Experimental

Materials and Methods. All silicon-containing organic compounds were purchased from Gelest and either used without further purification or distilled prior to use. Silicate minerals were obtained from several commercial sources. Organic solvents, inorganic salts, and catalysts were obtained from Aldrich and were used without further purification. All reactions were performed under an atmosphere of dry nitrogen. Flasks were oven-dried and allowed to cool in dry box prior to use. HPLC grade THF was dried and deoxygenated by passage through an alumina drying column prior to use. Air- and moisture-free manipulations were carried out in a Vac Atmospheres glove box.

Processing. Melt-processing of nanocomposites was performed on a DSM Micro 15 Compounder with a chamber free-volume of 15 cm^3. Polymers and nanomaterials were charged to the mixer in the appropriate amounts, and subjected to a residence time of five minutes under an inert nitrogen atmosphere. Blend extrudates were transferred to a DSM micro-injection molder for the fabrication of disks. Films were prepared by compressing sections of compounded extrudate in a Tetrahedron press between metallic platens and pieces of Kapton film for ease of subsequent film removal.

Characterization. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were obtained on a Bruker 400-MHz spectrometer. ^{1}H and ^{13}C NMR spectra of 10% w/v CDCl$_3$ solutions were obtained. ^{29}Si NMR spectra of 25% w/v CDCl$_3$ solutions were acquired. ^{13}C NMR spectra were obtained with broadband proton decoupling. A heteronuclear gated decoupling pulse sequence (NONOE) with a 10 sec delay was used to acquire ^{29}Si NMR spectra. Residual CHCl$_3$ was used as an internal standard for ^{1}H and ^{13}C NMR. ^{29}Si NMR spectra were referenced to internal TMS. Differential Scanning Calorimetry (DSC) experiments were performed on a TA Instruments Q100 using a nitrogen purge gas. Thermogravimetric Analysis (TGA) was performed on a TA Instruments TGA 2050 instrument at a flow rate of 40 cc of nitrogen or air per min. The temperature was increased 5 °C/min from 25 to 600 °C. Rheological measurements were obtained on an Anton Paar MCR 500 rheometer in parallel plate configuration (gap width = 1.5 mm). Dynamic mechanical analysis (DMA) was conducted on a TA Instruments Q800 instrument, using the film test fixture and nitrogen gas purge.

Results and Discussion

Silicon-containing compounds often impart desirable properties when blended into polymers and resins in which they are miscible. Any compound to be blended into the polymer must not only be highly miscible in the polymer, but must be thermally stable beyond the polymer processing temperature. Fortunately, most of these compounds degrade at temperatures near, or above, 400 °C. This high temperature stability allows the blending of many of these compounds to improve properties of various polymer systems. In addition to melt-blending, many can be chemically bound to the polymer backbone. This is often accomplished by the direct copolymerization of a hybrid monomer during polymerization and results in the hybrid compound being pendant to the polymer backbone. It has been observed that pendant POSS produce superior thermal and mechanical properties in the polymers to which they are attached than do similar polymers blended with POSS.

Conclusions

Improved oxidation-resistance is achieved in polymeric materials through the incorporation of silicon-containing compounds. These compounds are often organically-modified particles, such as silicas, clays, and silsesquioxanes, which can be mechanically blended into a wide variety of polymer matrices. In order to achieve improved dispersion of the silicon phase in thermoplastic polymers, it may be desirable for the silicon-containing compound to be covalently bound to the polymer backbone, which can be accomplished by polymerization of silicon-containing monomers, copolymerization, or grafting reactions. In thermosetting polymers, the covalent approach is preferred due to the ease of monomer processing and the low potential for phase separation during cure.

Acknowledgement. We gratefully acknowledge the Air Force Office of Scientific Research and the Air Force Research Laboratory, Propulsion Directorate for financial support.

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