Polyhedral Oligomeric Silsesquioxane Trisilanols as Dispersants for Titanium Oxide Nanopowder

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ABSTRACT: Trisilanol isobutyl polyhedral oligomeric silsesquioxane (POSS) was used to disperse nanosized titanium dioxide (TiO_2) particles in polypropylene (PP). The silanol groups of the POSS cage were bound to the surface of the TiO_2 particles, creating a layer of isobutyl POSS that improved compatibility with the PP matrix. POSS was an effective dispersant both when applied in a chemical pretreatment of TiO_2 and when simply added to the blend during melt compounding. The average particle size of TiO_2 was reduced from 70 nm for neat TiO_2 to 50 nm for the POSS/TiO_2 blend to 33 nm for TiO_2 chemically treated with POSS. Additionally, the POSS coating improved the color of the material and reduced the catalytic effect of TiO_2 on thermooxidative degradation. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 2503–2508, 2008

Key words: blends; coatings; electron microscopy; extrusion; nanotechnology

INTRODUCTION

Polymeric nanocomposites have been the subject of intense research interest over the past 15 years, spawned by advances such as the discovery of spherical fullerenes and carbon nanotubes and Toyota's initial commercialization of nylon/clay nanocomposite materials.[1,2] Nanofillers are projected to provide advanced performance capabilities for engineering polymer applications, imparting the high strength and modulus obtained with traditional fillers without their negative side effects, such as reduced processability and impact strength. Widespread commercialization of polymer nanocomposite materials, however, has been disappointingly slow, and in many cases, observed property enhancements fall far short of expectations, in large part because of the aggregation tendency and difficulty of dispersion of nanoparticles. Additional hurdles include the prohibitively high cost of manufacturing nanoparticles and nanocomposites and potential environmental hazards associated with some nanomaterials.[3–13]

Polyhedral oligomeric silsesquioxane (POSS) nanostructured chemicals (Fig. 1) provide a unique approach to the development of polymeric nanoengineered materials. POSS molecules are cagelike organic–inorganic structures described by the general chemical structure $RSiO_{1.5}$. As illustrated in Figure 1, POSS molecules consist of a Si—O—Si inorganic cage surrounded by an organic corona (represented by substituent R). The inorganic cage, with the structure $(SiO_{1.5})_n$ (where $n = 8$, 10, or 12), may be a fully condensed closed [Fig. 1(A)] or open [Fig. 1(B)] structure. The diameter of these monodisperse particles ranges from 1 to 3 nm, depending on the composition of the cage. The substituents can be varied widely to provide a range of different properties or to increase or reduce compatibility with a polymer matrix, or they can be made reactive to allow copolymerization or graft polymerization with a spectrum of monomers.

The first reference to POSS materials dates to 1946, when the molecules were first isolated via the thermolysis of the polymeric products produced from the cohydrolysis of methyltrichlorosilane with dimethylchlorosilane.[14] Extensive POSS research was performed at the Air Force Research Laboratory in subsequent years,[15,16] and in 1998, Hybrid Plastics (Hattiesburg, MS) was formed as a spin-off company to commercialize the technology. Today, over 150 different POSS molecules are produced commercially.[17] Besides olefins and molecular silicas, a wide variety of POSS molecules with functional groups ranging from halides, epoxies, silanols, and alcohols to acryl-
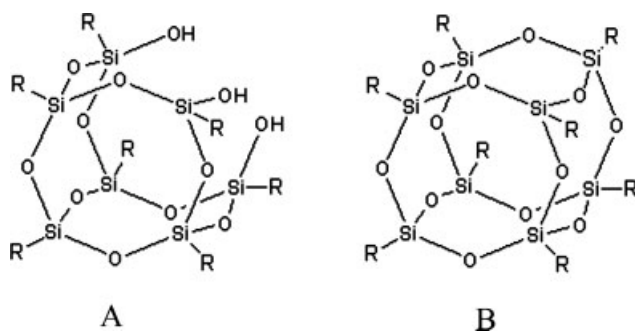
Figure 1 Generalized POSS structure: (A) open cage and (B) condensed (closed) cage.

ates and methacrylates are commercially available.[17] A large number of studies have been devoted to the chemical incorporation of POSS derivatives into polymer matrices via copolymerization or grafting.[18–20] Various POSS-based monomers and macromers have been synthesized, and a wide variety of POSS-based copolymers have been reported, including copolymers of polysiloxane,[21,22] polynorbornene,[23] polyurethane,[24,25] poly(methyl methacrylate),[26,27] epoxies,[28] and poly(4-methyl styrene).[29,30] In general, these copolymers exhibit organic/inorganic hybrid properties, demonstrating to various degrees enhanced modulus, stiffness, flame retardancy, and thermal stability in comparison with the base polymer.[31–34]

Although reactive POSS nanostructured chemicals can be readily dispersed in a polymer matrix at the molecular level through copolymerization, dispersion via simple melt mixing is desirable because of wide applicability and low manufacturing cost. This approach has been less studied, and fewer reports of melt-mixing nonreactive POSS in polymer matrices have appeared.[32–37] It is clear from these limited studies that the choice of the organic substituent is critical for the compatibility and dispersion of POSS in the polymer. For example, Zhao and Schiraldi[33] reported that trisilanol phenyl POSS, when blended with polycarbonate, yielded transparent blends with slightly improved modulus at POSS loading levels up to 5 wt %, whereas blends of polycarbonate with trisilanol isooctyl POSS at the same loading levels were opaque (this indicated poor dispersion).[33]

The ability to tailor POSS structures to achieve desired levels of dispersion in a polymer matrix suggests the possibility of using POSS nanostructured chemicals as dispersing aids for difficult-to-disperse nanoparticles. The current state of the art uses alkoxysilane coupling agents and various surfactants, such as stearates, to disperse particles.[38] POSS silanols possess several distinct advantages over the traditional approach. POSS silanols are stable in the silanol form, so they can applied directly in one step. Additionally, because POSS silanols do not

readily react with one another, only a monolayer of POSS will be deposited on the filler's surface with little possibility of oligomer and condensed particle formation. Three silanol groups per cage produce stronger, more robust bonds than typical coupling agents. Because of the enormous surface area to volume ratio of POSS, polymer–POSS interaction increases dramatically in comparison with coupling agents.

In this study, polypropylene (PP) blends with POSS and nanosized titanium dioxide (nano-TiO_2) particles were prepared via two methods: first, simple melt mixing of the individual materials, and second, chemical treatment of the nano-TiO_2 particles with reactive POSS molecules and then melt blending with PP. Titanium dioxide (TiO_2) was chosen as a model particle to test the theory of using POSS as a dispersant and surface treatment for metal oxides. Blend properties were evaluated via transmission electron microscopy (TEM), colorimetry, thermogravimetric analysis (TGA), and melt flow indexing.

EXPERIMENTAL

Materials

Nano-TiO_2 (with a nominal particle size of 21 nm) was obtained from Degussa (Ridgefield, NJ) (Aeroxide Titanium Dioxide P 25). PP was purchased from Ashland Distribution (Cincinnati, OH) (Hival 5250). Trisilanol isobutyl polyhedral oligomeric silsesquioxane (TSI–POSS) was manufactured by Hybrid Plastics (Hattiesburg, MS) and is a free-flowing white powder.

Sample preparation

Three types of nano-TiO_2 blends were prepared. The first type, uncoated nano-TiO_2, was prepared by the melt blending of as-received nano-TiO_2 particles into PP. The second type, a nano-TiO_2/POSS blend, was prepared by the melt blending of nano-TiO_2 and TSI–POSS with PP in desired compositions. For the third type, a POSS-treated nano-TiO_2 blend, nano-TiO_2 was first chemically treated with TSI–POSS and then melt-blended into PP. For the POSS chemical treatment, nano-TiO_2 (162 g), TSI–POSS (16.5 g), and hexanes (1350 g) were added to a 3-L, round-bottom flask. The flask was attached to a Buchi (New Castle, DE) rotovap and rotated for 1 h at atmospheric temperature and pressure. A vacuum was then applied to remove the hexanes. The solid, white powder was processed through a jet mill, and this resulted in a low-density white powder (110 g).

The melt blends were prepared with a B&P Process (Saginaw, MI) twin-screw extruder with 25-mm screws and a length/diameter ratio of 40:1 at a temperature of

225°C. PP and nano-TiO$_2$ were added by separate feeders at rates of 9 and 0.09 kg/h, respectively. The nano-TiO$_2$/POSS blend was prepared by the blending of TSI–POSS with PP at a 5 wt % loading followed by a second extrusion step in which nano-TiO$_2$ was added. Films for optical tests were prepared on a Carver (Wabash, IN) hydraulic melt press at 200°C.

Transmission electron microscopy/energy-dispersive X-ray (TEM–EDAX)

For TEM–EDAX analysis, a JEOL 2100 ultrahigh-resolution transmission electron microscope was employed (JEOL, Ltd., Tokyo, Japan) at an accelerating voltage of 200 kV. Ultrathin sections, 90–100 nm thick, were prepared by cryogenic ultramicrotoming of the samples with a glass knife with a Leica (Nussloch, Germany) EM UC6 cryomicrotome at −80°C. Subsequently, the ultrathin sections were collected on a 600-mesh copper grid. Elemental mapping of the ultrathin sections was performed with energy-dispersive X-ray analysis. Elemental maps were acquired with EDAX Genesis software.

Image analysis to determine the number of TiO$_2$ particles and particle sizes in each blend was performed with Microsoft Paint. The number of nanometers per pixel was calculated from the TEM images by the determination of the number of pixels in the scale bar and the division of this into the number of nanometers represented by the scale bar. One 1300 nm × 1300 nm sample image was randomly cut from each of the larger TEM images for each TiO$_2$ blend. The particle size was recorded by the counting of the particle width (X) and height (Y) in pixels. The values were converted to the length in nanometers with the aforementioned method, and the averages were calculated.

Optical characterization

A BYK Gardner (Columbia, MD) color-guide apparatus was used to perform color (*LAB*; ASTM E 308), opacity (ASTM D 2805), and yellowness index (ASTM E 313-98) measurements according to the ASTM methods indicated. A BYK Gardner haze–gloss instrument was used to perform haze and gloss readings according to the ASTM D 4039 and ASTM D 523 test methods, respectively.

### Thermal and melt flow characterization

The melt flow index (MFI) was obtained on a Dynisco (Franklin, MA) LMI D4004 at 230°C/2.16 kg in accordance with ASTM D 1238. TGA evaluations were conducted on a TA Instruments (New Castle, DE) Q500 at a heating rate of 20°C/min under a nitrogen atmosphere.

RESULTS AND DISCUSSION

To evaluate the effect of POSS on the dispersion of nano-TiO$_2$ in a polymer matrix, untreated nano-TiO$_2$ (with no organic surface treatment) was evaluated as a control. Silanols bind to metal oxide surfaces first by hydrogen bonding followed by covalent bonding if the proper conditions exist.[39] The first step involves hydrogen binding between the silanol and surface hydroxyl groups. Upon elimination of the water of the reaction, a covalent M—O—Si bond is formed. Assuming a nominal nano-TiO$_2$ particle size of 21 nm and a POSS surface coverage area of 1.6 nm^2 per POSS cage derived with molecular simulation, it has been calculated that 5 wt % POSS with respect to TiO$_2$ would be required to provide a monolayer coating that completely covered the nano-TiO$_2$ particle surface. Thus, to ensure an adequate amount of POSS for surface coverage, 10 wt % TSI–POSS with respect to TiO$_2$ was used in the coating process described in the Experimental section.

TGA was performed to verify and quantify the presence of TSI–POSS in the coated nano-TiO$_2$ (Fig. 2). Untreated nano-TiO$_2$ [Fig. 2(a)] showed minimal thermal degradation up to a temperature of 800°C. The nano-TiO$_2$ treated with 10 wt % TSI–POSS [Fig. 2(c)] exhibited an approximately 10% weight loss above 200°C that could be attributed to degradation of TSI–POSS. This sample was not washed before TGA, so the entire 10 wt % POSS could be observed. Figure 2(b) presents a treated nano-TiO$_2$ sample that was extensively washed with hexanes and tetrahydrofuran to remove any nonbound TSI–POSS. For this sample, an approximately 3% weight loss was observed, which is somewhat less than the calculated value of 5% POSS required for monolayer coverage. Most likely, there was not a high enough con-
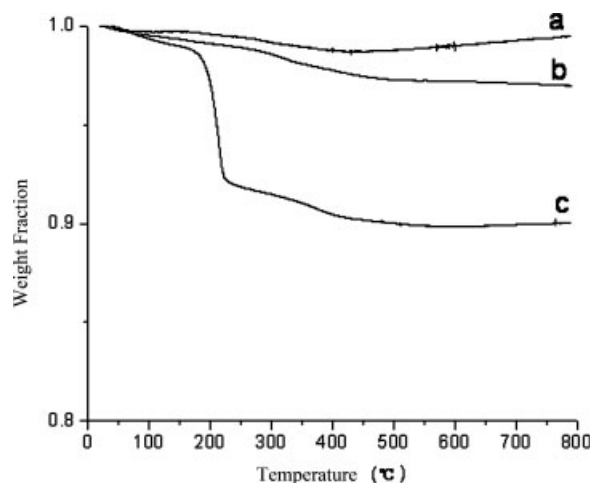
Figure 2 TGA of (a) untreated TiO$_2$, (b) POSS-treated TiO$_2$ after washing, and (c) POSS-treated TiO$_2$ before washing.
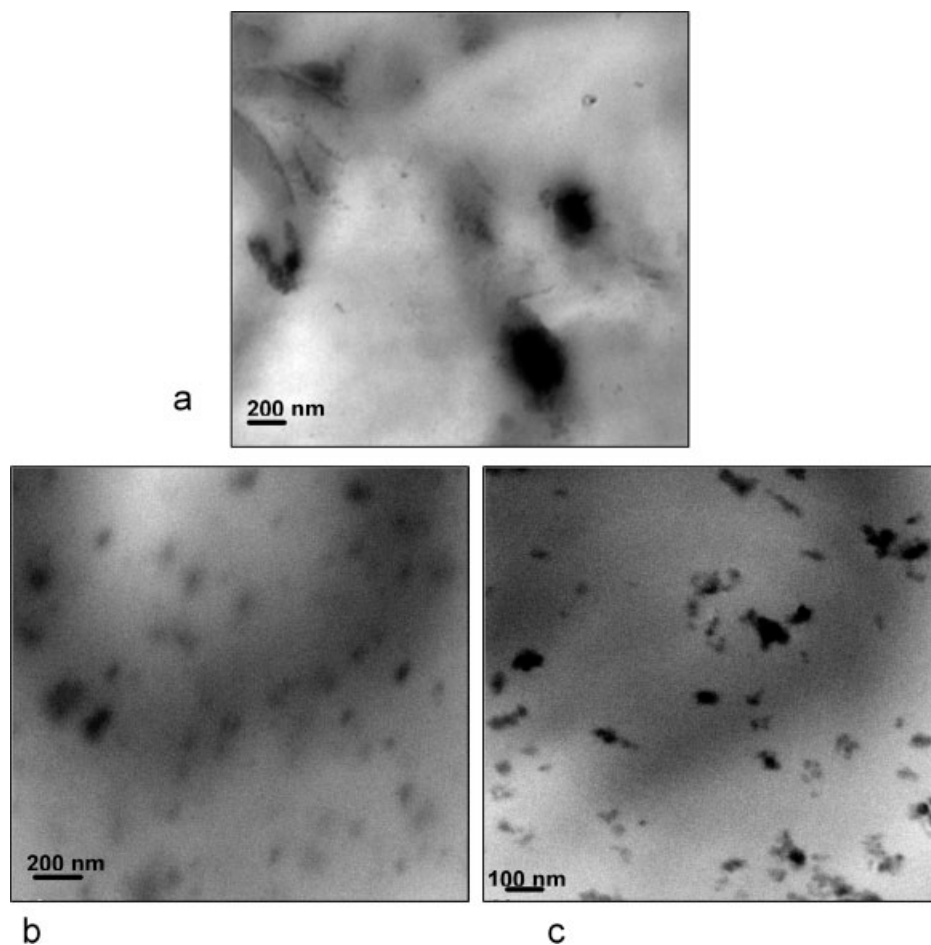
Figure 3 TEM images of PP/nano-TiO$_2$ blends with different TiO$_2$ treatments: (a) untreated nano-TiO$_2$, (b) a POSS/nano-TiO$_2$ blend, and (c) nano-TiO$_2$ chemically treated with POSS. Scale bars are indicated on each part of the figure.
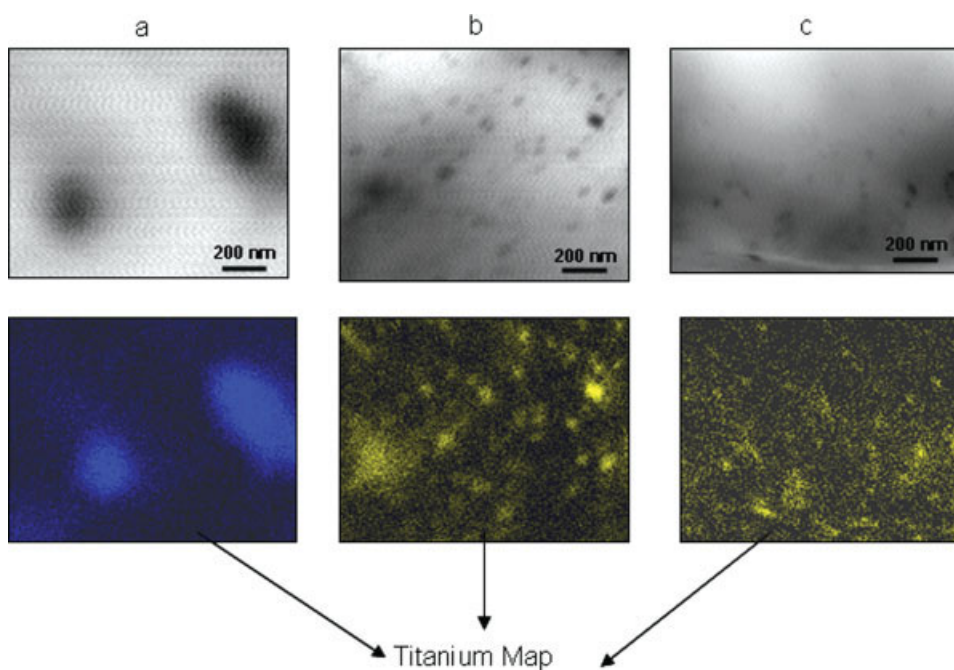
Figure 4 TEM–EDAX images of PP/nano-TiO$_2$ blends with different TiO$_2$ treatments: (a) untreated nano-TiO$_2$, (b) a POSS/nano-TiO$_2$ blend, and (c) nano-TiO$_2$ chemically treated with POSS. The scale bars represent 200 nm. The brightly colored areas indicate titanium. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

TABLE I
Average Particle Diameter for Nano-TiO₂ with Different Surface Treatments After Dispersion in the PP Matrix

	Sample		
	Untreated TiO$_2$	POSS/ TiO$_2$ blend	Chemically treated POSS/TiO$_2$
Average particle diameter (nm)	70.4	50.1	33.2
Standard deviation	31.9	21.4	11.6

centration of hydroxyl groups on the surface of the TiO$_2$ to obtain complete coverage. The fact that 3% POSS was retained after washing indicates the formation of a strong bond, probably covalent, between POSS and TiO$_2$.

Different TiO$_2$ treatment conditions yield dramatic differences in TiO$_2$ dispersion in PP, as observed by TEM analysis (Figs. 3 and 4). Figure 3(a–c) shows TEM micrographs of untreated nano-TiO$_2$, a nano-TiO$_2$/POSS blend, and nano-TiO$_2$ chemically treated with POSS, respectively, melt-blended in PP. Although TiO$_2$ aggregates greater than 200 nm in diameter were observed for the untreated nano-TiO$_2$, smaller, more highly dispersed particles were observed for the nano-TiO$_2$/POSS blend, and even smaller particles were observed for the POSS-treated nano-TiO$_2$ [note that the scale bar for Fig. 3(c) is 100 nm, whereas it is 200 nm for Fig. 3(a,b)]. Image analysis indicates that both the average particle size and the particle size distribution decrease with the POSS surface treatment in the order of untreated nano-TiO$_2$ > the nano-TiO$_2$/POSS blend > nano-TiO$_2$ chemically treated with POSS (Table I), with the particles chemically treated with POSS showing roughly half the size and polydispersity of the untreated particles. We hypothesize that POSS aids in the dispersion of the TiO$_2$ by its interaction with both the TiO$_2$ and the PP matrix. Previous studies have shown a high level of isobutyl POSS dispersion in a PP matrix, and this has been attributed to the isobutyl R group of POSS matched to the polarity and chemical structure of PP.[37] In this case, a POSS structure with silanol groups on one corner can bind to the polar TiO$_2$ particles, whereas the nonpolar isobutyl R group of POSS interacts via van der Waals forces with PP. The TEM data indicate that POSS added in the melt aids in TiO$_2$ dispersion. Premixing TiO$_2$ with POSS in a solution provides a greater opportunity for a chemical reaction between the molecules and results in smaller, more highly dispersed nano-TiO$_2$ particles in the melt.

Further evidence of the effect of POSS on the nano-TiO$_2$ dispersion can be observed by an analysis of the color, yellowness index, and haze of films prepared from the blends (Table II). Films produced from blends containing POSS were visibly whiter and less yellow than those prepared from the neat TiO$_2$, as quantified by the yellowness index and *LAB* values (Table II), with yellowness measurement in the decreasing order of untreated nano-TiO$_2$ > nano-TiO$_2$/POSS blend > nano-TiO$_2$ chemically treated with POSS. Haze and gloss exhibit the same trend, decreasing in value with the POSS treatment. Opacity measurements show no apparent trend. The decrease in haze can be explained by the decrease in the particle size of TiO$_2$ aggregates observed in TEM studies. The reduction in yellowness is explained by the fact that POSS coats the surface of the TiO$_2$ particles, making them less reactive to the PP matrix and resulting in reduced discoloration.[40]

TABLE II
Optical Properties of the Blends with Different TiO₂ Treatments

Test method		Sample		
Color, (LAB) Axis	(ASTM E 308) Background	Untreated TiO$_2$	POSS/ TiO$_2$ blend	Chemically treated POSS/TiO$_2$
L	91.8	90.2	89.7	90.1
A	−1.16	−1.54	−1.11	−1.09
B	5.95	7.64	6.83	5.24
Yellowness index (ASTM E 313-98)		14	12	9
Haze (ASTM D 4039)		164	130	119
Standard deviation		32	22	11
Opacity (%; ASTM D 2805)		38	44	37
Gloss (ASTM D 523)				
20°		2.5	2.0	1.7
60°		23.0	18.0	15.0
85°		43.0	39.0	36.0

The background values for *L*, *A*, and *B* were 91.8, −1.16, and 5.95, respectively.

TABLE III
MFI Values of the Blends with Different TiO$_2$ Treatments

Sample	MFI (g/10 min)	Standard deviation
Neat PP	18.8	0.2
PP with 1% uncoated TiO$_2$	31.4	0.2
PP with 5% POSS	24.5	0.4
PP with a 1% TiO$_2$/5% POSS blend	25.7	0.2
PP with 1% POSS-coated TiO$_2$	20.9	0.4

The protective coating effect of POSS was further exhibited in melt flow studies (Table III). Although the blend of uncoated TiO$_2$ showed a 70% increase in MFI (from 18.8 for neat PP to 31.4 for the uncoated TiO$_2$ blend), POSS-treated TiO$_2$ showed only a minor increase in MFI (from 18.8 to 20.9). The large increase in MFI for the uncoated TiO$_2$ blend indicates acceleration of the thermal oxidative degradation of the PP matrix in the presence of the uncoated TiO$_2$,[38] which was further evidenced by the increase in the yellowness index of this blend. Treatment of TiO$_2$ with POSS in solution largely eliminates this effect. Blends of POSS with TiO$_2$ in the melt exhibit intermediate behavior.

CONCLUSIONS

POSS silanols have successfully been used as dispersing agents for nano-TiO$_2$ particles in PP. Chemically treating TiO$_2$ with POSS in a solvent solution was more effective than adding untreated TiO$_2$ and POSS directly into a melt compounder. POSS treatment reduced the TiO$_2$ agglomerate size in PP from 70 to 33 nm by functioning as a compatibilizing agent, in which the silanol groups of the POSS cage were bound to the TiO$_2$ particle and surrounded it with a high-surface-area structure of nonpolar isobutyl groups.

The effects of POSS observed in this study are believed to be generic for metal oxide surfaces and can be used in many other applications. Because of its nanostructured topography, POSS has a distinct advantage over traditional silane coupling agents by dramatically increasing the surface area of the treated particle. A direct comparison between POSS and traditional dispersants is currently being studied.

References

1. Calvert, P. Carbon Nanotubes: Preparation and Properties; CRC: Boca Raton, FL, 1997; p 277.
2. Okamoto, M. Rapra Rev Rep 2003, 14(7), report 163. http://www.rapra.net/products_and_services/Books/Materials/Composites/PolymerLayered_Silicate_Nanocomposites.asp (accessed July 2007).
3. Alexandre, M.; Dubois, P. Mater Sci Eng R: Rep 2000, 28(1–2), 1.
4. Chow, W. S.; Ishak, Z. A.; Mohd, K.; Kocsis, J. J Polym Sci Part B: Polym Phys 2005, 43, 1198.
5. Hadal, R.; Nathani, H.; Tanniru, M.; Misra, R. D. K. Annu Tech Conf Soc Plast Eng 2005, 63, 1444.
6. Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Kurauchi, T.; Kamigaito, O. J Polym Sci Part A: Polym Chem 1993, 31, 983.
7. Okada, A.; Usuki, A. Mater Sci Eng C 1995, 3(2), 109.
8. Usuki, A.; Kojima, Y.; Kawasumi, M.; Okada, A.; Fukushima, T.; Kurauchi, T.; Kamigaito, O. J Mater Res 1993, 8, 1179.
9. Yano, K.; Usuki, A.; Okada, A.; Kurauchi, T.; Kamigaito, O. J Polym Sci Part A: Polym Chem 1993, 31, 2493.
10. Lan, T.; Pinnavaia, T. J Chem Mater 1994, 6, 2216.
11. Wang, Z.; Pinnavaia, T. J Chem Mater 1998, 10, 1820.
12. Favier, V.; Canova, G. R.; Shrivastava, S. C.; Cavaille, J. Y. Polym Eng Sci 1997, 37, 1732.
13. Chazeau, L.; Cavaille, J. Y.; Canova, G.; Dendievel, R.; Boutherin, B. J Appl Polym Sci 1999, 71, 1797.
14. Scott, D. W. J Am Chem Soc 1946, 68, 356.
15. Phillips, S. H.; Haddad, T. S.; Tomczak, S. J. Curr Opin Solid State Mater Sci 2004, 8, 21.
16. Mabry, J. M.; Vij, A.; Iacono, S. T.; Grabow, W. W. Polym Prepr (Am Chem Soc Div Polym Chem) 2005, 46, 630.
17. http://www.hybridplastics.com (accessed July 2007).
18. Lichtenhan, J. D. Comments Inorg Chem 1995, 17, 115.
19. Shockey, E. G.; Bolf, A. G.; Jones, P. F.; Schwab, J. J.; Chaffee, K. P.; Haddad, T. S.; Lichtenhan, J. D. Appl Organomet Chem 1999, 13, 311.
20. Lee, A.; Lichtenhan, J. D. J Appl Polym Sci 1999, 73, 1993.
21. Lichtenhan, J. D.; Vu, N. Q.; Carter, J. A.; Gilman, J. W.; Feher, F. J. Macromolecules 1993, 26, 2141.
22. Mantz, R. A.; Jones, P. F.; Chaffee, K. P.; Lichtenhan, J. D.; Gilman, J. W.; Ismail, I. M. K.; Burmeister, J. Chem Mater 1996, 8, 1250.
23. Mather, P. T.; Jeon, H. G.; Romo-Uribe, A.; Haddad, T. S.; Lichtenhan, J. D. Macromolecules 1999, 32, 1194.
24. Turri, S.; Levi, M Macromolecules 2005, 38, 5569.
25. Turri, S.; Levi, M. Macromol Rapid Commun 2005, 26, 1233.
26. Patel, R. R.; Mohanraj, R.; Pittman, C. U. J Polym Sci Part B: Polym Phys 2005, 44, 234.
27. Lichtenhan, J. D.; Otonari, Y. A.; Carr, M. J. Macromolecules 1995, 28, 8435.
28. Lee, A.; Lichtenhan, J. D. Macromolecules 1998, 31, 4970.
29. Romo-Uribe, A.; Mather, P. T.; Haddad, T. S.; Lichtenhan, J. D. J Polym Sci Part B: Polym Phys 1998, 36, 1857.
30. Haddad, T. S.; Lichtenhan, J. D. Macromolecules 1996, 29, 7302.
31. Zheng, L.; Farris, R. J.; Coughlin, E. B. Macromolecules 2001, 34, 8034.
32. Fu, B. X.; Hsiao, B. S.; Pagola, S.; Stephens, P.; White, H.; Rafailovich, M.; Sokolov, J.; Mather, P. T.; Jeon, H. G.; Phillips, S.; Lichtenhan, J.; Schwab, J. Polymer 2001, 42, 599.
33. Zhao, Y.; Schiraldi, D. A. Polymer 2005, 46, 11640.
34. Fina, A.; Tabuani, D.; Frache, A.; Camino, G. Polymer 2005, 46, 7855.
35. Kopesky, E. T.; McKinley, G. H.; Cohen, R. E. Polymer 2006, 47, 299.
36. Joshi, M.; Butola, B. S.; Simon, G.; Kukaleva, N. Macromolecules 2006, 39, 1839.
37. Misra, R.; Fu, B.; Morgan, S. E J Polym Sci Part B: Polym Phys 2007, 45, 2441.
38. DeArmitt, C.; Rothon, R. Plast Additives Compd 2002, 4, 12.
39. Arkles, B. Chemtech 1977, 7, 766.
40. Gachter, R.; Muller, H. Plastics Additives Handbook, 4th ed.; Hanser/Gardner: Cincinnati, OH, 1993; Chapters 1 and 11.