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Polyimide–Organosilicate Hybrids with Improved Thermal and Optical Properties

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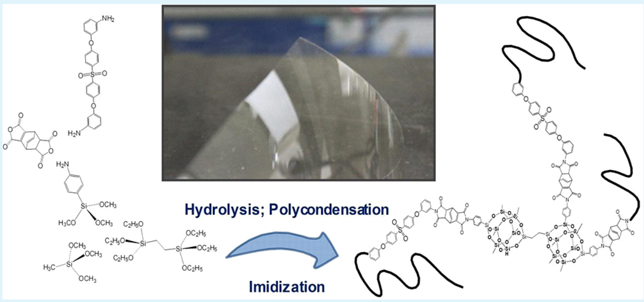
Supporting Information

ABSTRACT: Through hydrolysis and polycondensation of amino-silane with alkyl bridged silane, a new type of polysilsesquioxane (PSSQ) was obtained. Here we use amine functionalized silane and bis(silyl)ethane to synthesize alkyl chain linked PSSQ. Compared to conventional polyhedral oligomeric silsesquioxane (POSS), this new silane compound has both enhanced thermal stability and improved compatibility with poly(amic acid). Gelation of this silane compound with poly(amic acid) provides polyimide–organosilicate composite materials. We show that films made from solutions of the composites exhibit higher optical transparency and superior dimensional stability during thermal treatment than films of pure polyimide or of polyimide composites with conventional POSS. Bridging of POSS and chemical bonding between POSS and polyimide chains significantly enhance the physical properties. These results provide useful information for designing molecular architecture for the fabrication of high-performance plastic substrates in the future display devices.



KEYWORDS: *bridged-organosilicate, colorless polyimide, thermal expansion, optical transparency*

INTRODUCTION

A substrate is a critical component in display devices. It determines the devices' performance and reliability because operating thin film transistors are deposited on it.[1−7] Current glass or silicon wafer substrates, which have superior optical transparency or thermal stability, are one of the heaviest parts in display devices.[6,7] The form factors of future mobile devices are changing in various and rather practical ways to satisfy ubiquitous information obtaining environment. This includes replacing inorganic substrates with thin and light plastic substrates, which is necessary to fully exploit the many advantages that plastic displays can offer.[1−10]

Future substrates will require the high thermal and desirable optical properties presently found in inorganic substrates. The most widely used glass substrates are rigid, fragile, and relatively heavy, even though they are highly transparent and thermally stable.[8,9] Among plastic substrates, polyethylene naphthalates, poly(ethylene terephthalate), poly(ether sulfones), and polycarbonates are known as promising candidates because of their optical transparency, as high as current glass substrates.[11,12] However, they need to be improved in heat resistance and dimensional stability. In contrast, aromatic polyimides have excellent thermal stabilities and chemical resistance, though they have a yellowish color problem that makes them less applicable for optical components. Most polyimides show strong absorption between the UV- and visible-light region, rendering their color close to yellow or brown. This color is known to originate from the easy formation of inter- or intramolecular charge transfer (CT) complexes in polyimide chains.[13−17]

Previously, various ways of reducing the concentration of CT complexes were reported. To minimize interactions between the polymer chains, bulky side groups have been inserted into polyimide backbones.[18,19] Using kinked structured monomer units is analogous to reducing the concentration of CT complex formations.[20−22] Another way to obtain colorless polyimides is by manufacturing composite materials of polymer and inorganic materials. Such composites include organo-clay,[23] boron nitride,[24] and organosilicates.[25−27] Sometimes, diverse agents to aid in dispersing the inorganic components into the polymer matrix are necessary.[25,28] This procedure can reorganize and disorder the molecular structure which might also lessen CT complex concentrations. However, low miscibility between the polymer and the inorganic components or the dispersing agents can inhibit the polymer from exhibiting optimal physical properties.[23−28]

In this report, we introduce amine functionalized and alkyl bridged silane compounds that have enhanced dimensional stability and improved compatibility with polyimide chains. Polysilsesquioxanes (PSSQs), such as polyhedral oligomeric

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silsesquioxane (POSS), result from the hydrolysis and polycondensation of alkoxysilane and have been used widely for microelectronic applications, owing to their high thermal stability as well as low dielectric properties.[29,30] Employing such compounds in a polymer matrix can be an effective way to increase both the optical transparency[25,31] and thermal stability of polyimides.[26,32−35] Here we employ silsesquioxanes linked with alkyl chains and amino-silane monomers to obtain alkyl chain bridged amino-polyhedral oligomeric silsesquioxanes (ABA-POSS). These compounds have high dimensional stability and are compatible with polyimide precursors. Through condensation and imidization reactions, we obtained polyimide composites containing ABA-POSS that show both improved optical and thermal properties as compared to single cage-structured POSS or amine functionalized POSS.

EXPERIMENTAL SECTION

Monomers for Organosilicates and Poly(amic acid). Aminopropyl(trimethoxy)silane (APhTMS), bis(triethoxysilylethane) (BTSE), and methyl(trimethoxysilane) (MTMS) for alkyl chain bridged amino-polyhedral oligomeric silsesquioxane (ABA-POSS) compounds were purchased from Gelest, Inc. As dianhydride and diamine, which are precursors of poly(amic acid) (PAA), bicyclo-[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (BTDA) and 2,2-bis[4-(3-aminophenoxy) benzene] (*m*-BAPS), purchased from Sigma Aldrich Co., were used. Dimethyl acetamide (DMAc), DMF, and THF solvent were also purchased from Sigma Aldrich Co. As reference organosilicates, octa-isobutyl POSS and octa-aminophenyl POSS were purchased from Hybrid plastics, Inc. The chemical structures of silane compounds are shown in Figure 1.

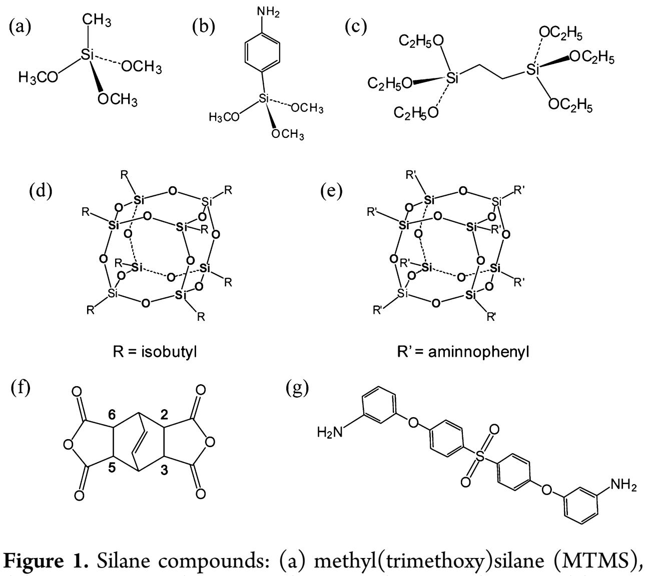


Figure 1. Silane compounds: (a) methyl(trimethoxy)silane (MTMS), (b) aminophenyl(trimethoxy)-silane (APhTMS), and (c) bis-(triethoxysilylethane) (BTSE). Commercial polyhedral oligomeric silsesquioxanes: (d) octaisobutyl-poss (T_8) and (e) octaaminophenyl-poss (A-T_8). Precursors for polyimide: (f) bicyclo-[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (BTDA) and (g) 2,2-bis[4-(3-aminophenoxy) benzene] (*m*-BAPS).

Oligomeric Organosilicate Compound Syntheses. Concentrations of 30 wt % APhTMS (9.58g, 0.045 mol) and 30 wt-% BTSE (5.31 mg, 0.015 mol) solutions in THF are added and agitated in a 250 mL round-bottomed flask in a presence of 30 wt-% MTMS (22.44g, 0.17 mol) solution in THF for ~1 h at 0 °C. Molar ratio of BTSE:APhTMS:MTMS is 1:3:11. After adding 0.02 mL of deionized water and 0.1 mL of 35 wt % HCl, the solution was stirred 5 h at 60 °C. All the reactions were controlled by reflux method under a regulated N_2 purge. After precipitation of the product with excess diethylether, the resulting solution was filtered and dried in vacuum giving white colored powder. The yield was ~64% with respect to the initial mass of total silane compounds.

Polymer Composite Synthesis. Synthesized ABA-POSS (10.2 mg or 20.4 mg) are inserted and agitated in a round-bottomed flask in the presence of 10 wt % BTDA (3.72g) solution in DMAc for about 1 h at 0 °C and 5 h in ambient temperature, ~25 °C. Subsequently, 10 wt % *m*-BAPS (6.48g) solution in DMAc is added thereto and agitated for 17 h to obtain PAA. All the reactions were controlled by reflux method under a regulated N_2 purge. Here, the concentrations of ABA-POSS are 1 or 2 wt % comparing to the total weight of initial mass of solids precursors. The same procedures are repeated for each of octa-isobutyl POSS and octa-aminophenyl POSS to obtain reference polymer composite materials.

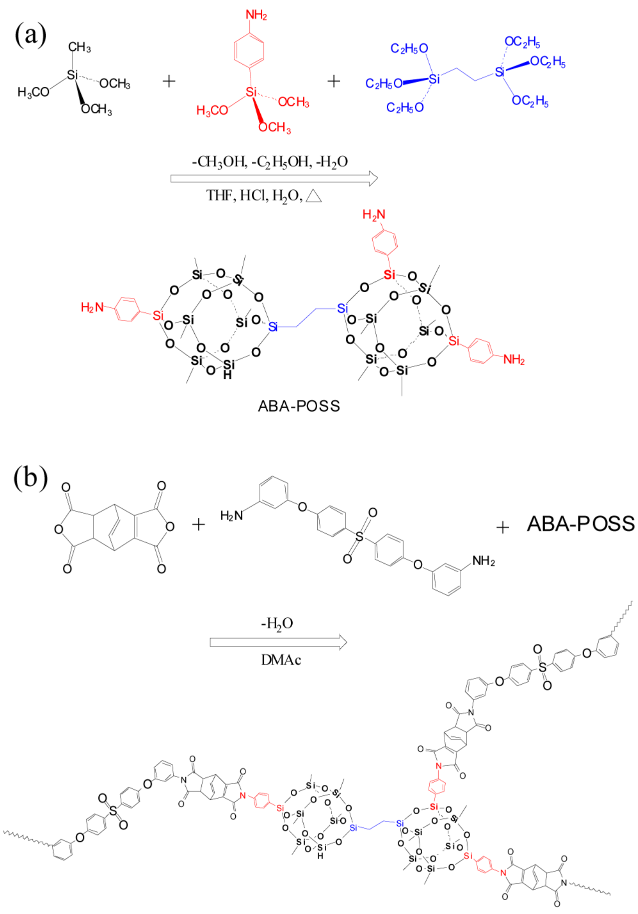
Film Fabrication. Using a 10 mL glass syringe, we dropped around 5 mL of the synthesized solutions onto glass substrates treated with octyl-trichlorosilane (OTS), as depicted in a previous report.[36] The glass substrates were cleaned with Jelight ultraviolet-ozone cleaner, deionized water, and nitrogen gas blowing. After OTS passivation by immersing in 0.02 mol L^{-1} OTS solution in hexadecane for 16 h, the substrates were sonicated with chloroform, isopropyl alcohol, and deionized water for 10 min each, and finally baked at 150 °C for 10 min under N_2 flow. Water contact angles of the substrates were ~110°. To prepare homogeneous film thickness, we employed a flow-coating technique, as introduced in a previous report.[37] Here the PAA solutions were applied onto glass substrates temporarily adhered to a custom-built, motorized translation stage. Film thickness was controlled by adjusting the lip gap of a metal blade to ~250 μm. After the solution was cast by sweeping the metal blade in one direction, the heating stage was set to 50 °C for 1 h for leveling and 80 °C for 1 h for removing the solvent under N_2 flow. Films atop glass plates were thermally heated up to 250 °C with ramping rates of 2 °C/min under N_2 flow. The films atop the glass substrates of low surface energy were easily released with an initiation of removal at one edge of the film with a razor blade.

Characterization. Molecular structure of synthesized ABA-POSS, commercial oligomeric organosilicates, and ABA-POSS reacted with only *m*-BAPS were explored with Bio Rad FTS-6000 FT-IR spectrometer. Molecular weight and its distribution were analyzed with Waters GPC 2690 with PS standards and Bruker Ultraflex III TOF/TOF 200 MALDI-TOF MS. Hitachi FE-SEM 4500 was used to obtain SEM image of ABA-POSS. Glass transition temperature (T_g) of of each polyimide with organosilicate hybrid films was measured with TA Instruments' DSC Q2000 under N_2 purge. Coefficient of thermal expansion (CTE) was measured with TA Instruments' TMA 2920. Films were cut in to 5 mm ×20 mm rectangular shapes and scanned with 5 °C/min heating rate under N_2 flow. Films were cut in to ≈20 mm ×20 mm size and their optical transparencies, such as yellow index (YI) and UV−vis absorbance, were measured with a CM3600D spectrophotometer manufactured by KONICA MINOLTA Inc. under N_2 purge. The thermal stability of hybrid films was measured with TA Instruments TGA Q5000IR, ramping rate of 10 °C/min and under N_2 flow. Mechanical properties of the hybrid films were investigated with universal testing machine (UTM) manufactured by Simatsu Company in air.

RESULTS AND DISCUSSION

Hydrolysis and Polycondensation of Silane Compounds. Obtaining polyimide−organosilicate composite materials requires a sol−gel process consisting of two steps. The first step is hydrolysis and polycondensation of silane compounds to obtain PSSQ and the second step is condensation and imidization of PSSQ with polyimide precursors.[33] Silane monomers used in the first step are shown in Figure 1a−c. These three monomers contain alkoxy functional groups. Through hydrolysis, silanol groups are formed. When the silanol reacts with the alkoxy groups, alcohol is produced and finally forms PSSQ through polycondensation reactions, as represented in Scheme 1a.

Scheme 1. (a) Possible Chemical Structure of ABA-POSS and Its Synthesis through Hydrolysis and Polycondensation of Silane Compounds; (b) Fabrication of Polyimide−Organosilicate Composite through Condensation and Imidization[a]



[a] The molecular structure of polyimide−organosilicate in b represents one of the examples.

This synthesis condition was maintained as the optimal condition for cage structure, usually denoted as T_n, forming. Hydrolysis is generally minimized at pH 7 and polycondensation is minimized at pH ~4.2 (pK_a = 9.5).[38,39] Therefore, we added dilute HCl to stimulate the initiation of reactions. Cage structure formation after hydrolysis and a certain extent of condensation is due to reactions of internal functional groups in intramonomers. So there should be optimal concentration that slow the polycondensation between intermonomers.[38,40,41] In this paper, the initial concentration of the reaction solution is around 30 wt %.

The target structure of PSSQ in this report is shown in Scheme 1a, ABA-POSS. Certainly, ABA-POSS may have partial cages when it is formed after solution reaction. Two distinctive features of this compound are that it contains amine functional groups and two cages are connected with an alkyl bridge. Amine groups are able to react with dianhydrides, one of the major components in polyimide, to form imide bonds. This indicates that compatibility between the amino PSSQ and polyimide could be increased, compared to adding unreactive PSSQ into the polymer matrix.[26,32,34]

The alkyl bridge, in particular, is related to dimensional stability. Cage structured POSSs are hard materials that have high thermal stability as well as many promising physical properties for microelectronic applications.[38−49] In some cases, however, POSS like materials with a thermal expansion coefficient (CTE) higher than 50 ppm/°C were reported.[51,51] This is assumed to originate in the unfavorable packing structures of POSS.[50] Also, a large number of end groups, such as eight alkyl groups connected to cube vertice Si in the case of T_8, are able to move thermally. This gives negative influences, which raises CTE. According to previous reports,[41,50] alkyl bridges increase the extent of network and density, and the latter plays a more critical role in lowering the CTE.

For the formation of an ABA-POSS, one BTSE, two or three APhTMS, and ten to eleven MTMS monomers are required, as can be counted in Scheme 1a. Other commercial silane monomers, such as methyl-triethoxysilane, aminopropyl triethoxysilane, and so on, can be used in hydrolysis and polycondensation reactions. Three APhTMS potentially enables cross-linking when ABA-POSS is inserted in polyimide chains.

Chemical Structure of Alkylbridged Polysilsesquioxane. The chemical structure of ABA-POSS was verified with FT-IR. Here we have used two commercial cage-structured PSSQs as references for the comparison of physical properties, when the PSSQs are hybridized with polyimides. Figure 2

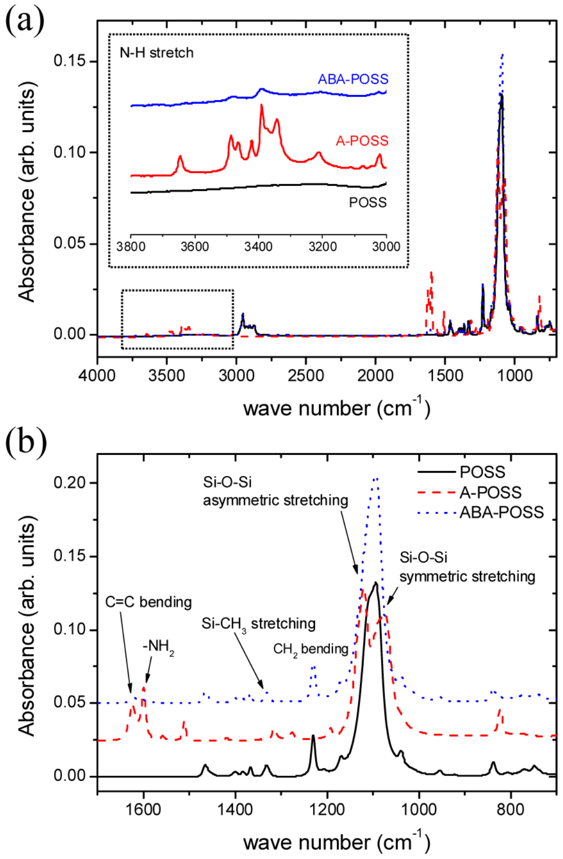


Figure 2. FT-IR spectra for octaisobutyl-poss (POSS), octaamino-phenyl-poss (A-poss), and ABA-POSS. (a) Full spectrum and enlargement of 3000−3800 cm^{-1}; (b) 700−1700 cm^{-1}. Data in b and inset in a are off set for clarity.

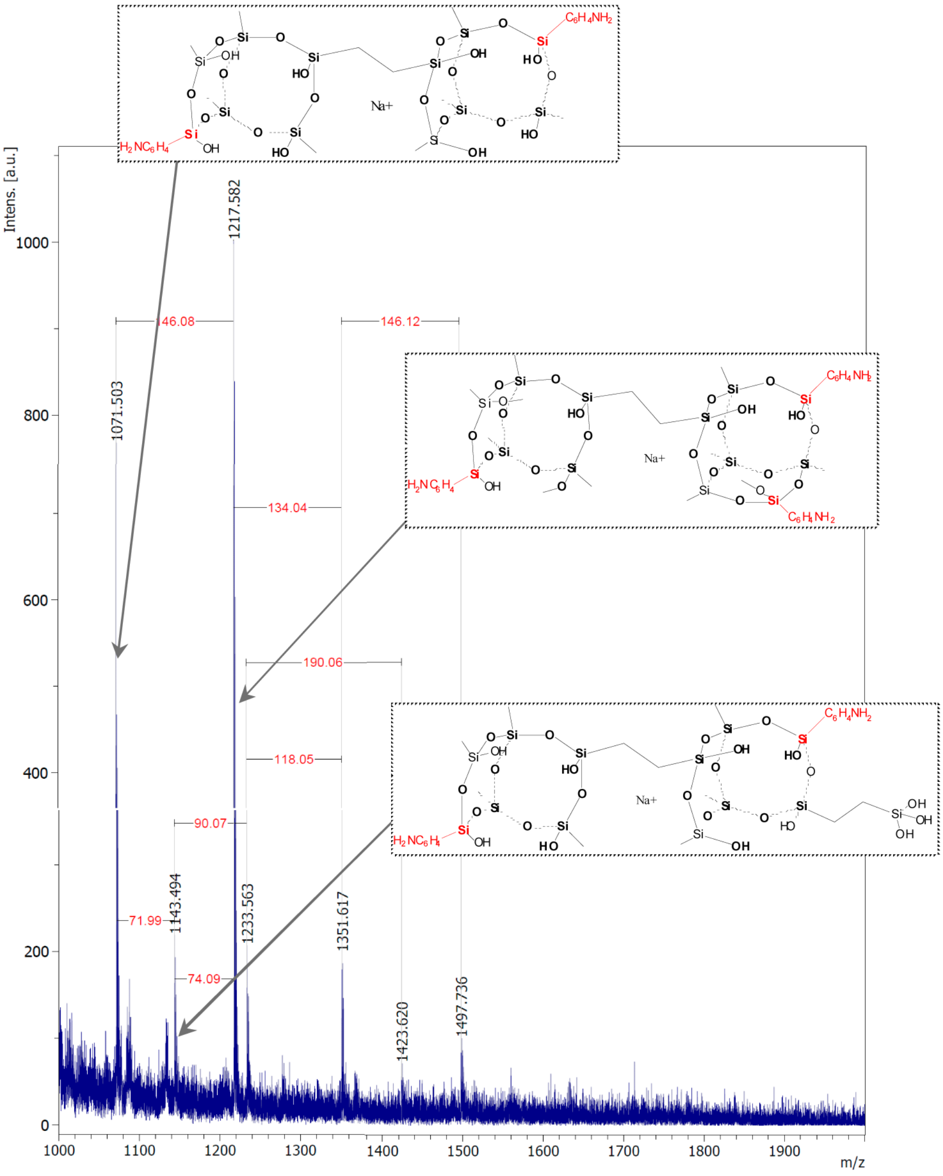


Figure 3. MALDI-TOF mass spectrum of synthesized PSSQ and the probable molecular structure of ABA-POSS.

shows the spectrum of ABA-POSS and commercial octaisobutyl-POSS (denoted as POSS) and octaaminophenyl-POSS (denoted as A-POSS). Their structures are depicted in Figure 1d, e. The absorption band associated with N−H stretching mode (inset in Figure 2a) is not detected in POSS, but it is clearest in A-POSS, which has octaamino groups per one molecule. There is a weak N−H stretching mode in ABA-POSS (dotted line). All three PSSQs show high intensity absorption bands associated with Si−O−Si stretching mode at ∼1050−1150 cm^{-1} (Figure 2b).[52] The peak split in A-POSS indicates the cage structure is less perfect and has small cages due to bulky aminophenyl groups in every vertex of a cage. In accordance with the chemical structure of the monomers used, absorption bands associated with Si-CH_3 stretching and CH_2 bending mode at ∼1340 cm^{-1} and ∼1220 cm^{-1}, respectively, are detected only in POSS and ABA-POSS. They may come from isobutyl end groups in POSS and ethylene bridges in ABA-POSS.

Molecular Weight and Structure of Alkylbridged Polysilsesquioxane. Polycondensation of silane compound can give rise to POSS as well as other oligo-PSSQ and infinite network gels, according to reaction conditions.[38,39] In particular, various kinds of forms are possible in oligomeric PSSQs. Specifically, given the size of organic substituent in silane compounds, closed cage-type structures are more likely to form, due to the steric hindrances.[40] One effective way to predict the exact molecular structures of the reaction product is by measuring the molecular weight. First, molecular weight distribution of the product was measured with GPC and it ranged from 800 to 4000 (S1 in the Supporting Information). Figure 3 shows matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) data for sodium adduct ions of PSSQs polymerized for 5h, and probable chemical structures of dumbbell shaped PSSQs are presented. Here two values of Da (1 Da ≈ 1.66 × 10^{-24} g) increment are noticeable. The Da increase of ∼72 largely originates from the addition of a BTSE ethyl branch and the Da increase of ∼146 corresponds to an APhTMS functional group. All conjectural structures are partial cagelike on account of being obtained from reaction solution. During thermal annealing of their composite films, it is expected that the partial cages would be condensed further through intramolecular condensations.[38−41]

Polymerization and Imidization of Polyimide−Organosilicate Composite Materials. As introduced, aromatic polyimide is one of the most promising candidate materials for future display substrates. Here we employed polyimide precursors, BTDA and *m*-BAPS, dianhydride, and diamine, respectively (Figure 1f, g). BTDA has unsaturated carbons in cyclic rings, but it is thermally stable and is resistant to ring-opening by common organometallic catalysts. The stability comes from its stereochemistry.[53] BTDA can be synthesized from the reaction of 2*H*-pyran-2-one with maleic anhydride, which includes Diels−Alder reactions.[54,55] Here, prepared BTDA has a five membered ring of anhydride in both sides only with endoconfiguration by the central double bond. Accordingly, hydrogens at 2, 3, 5, and 6 (Figure 1f) come to have exopositioning. In this configuration, metal catalysts with bulky organic ligands are highly limited in access to the double bond. In polyimide chains, the protruding double bonds are able to lessen the intermolecular interactions between the polymer chains. Flexible and kinked structured *m*-BAPS, which has amine functional groups in meta-positions, is also favorable to minimize the charge transfer interactions between the polymer chains. In this respect, polyimidse composed of BTDA and *m*-BAPS present higher transparency compared to conventional polyimides.[37]

In Scheme 1b, the target molecular structure of polyimide composite with ABA-POSS is presented. The final product has both the imide ring connected with *m*-BAPS and connected with APhTMS, which makes it difficult to characterize the difference in the molecular structure of the composite from the neat polyimide. Instead, the precursor for the ultimate polymer composite, ABA-POSS reacted only with BTDA, was characterized with FT-IR (S2 in the Supporting Information). The concentrations of ABA-POSS in the polymers are 1 and 2 wt %. For comparison, other polyimide-conventional POSS composites (Figure 1d, e) are prepared through the same procedure.

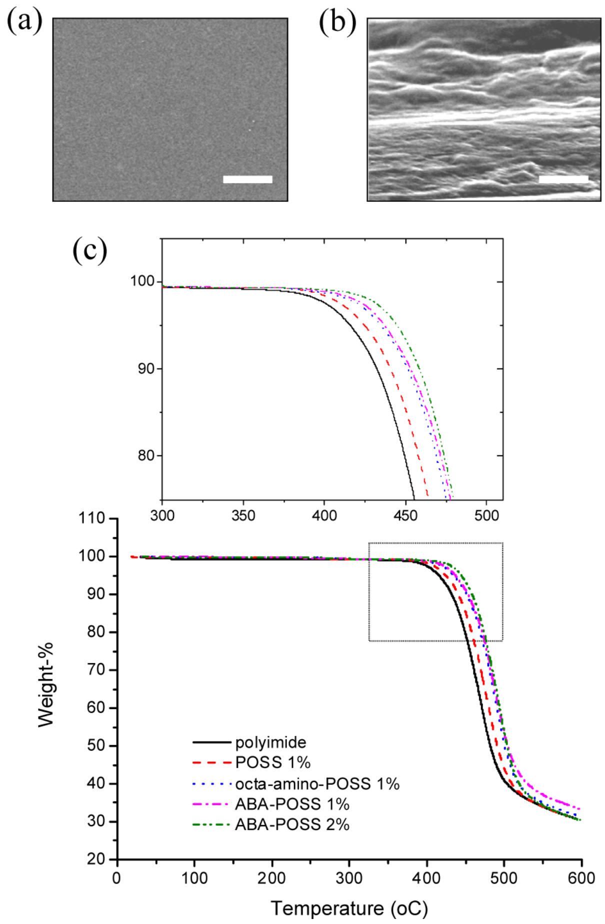


Figure 4. (a) SEM surface image and (b) cross-section image of polyimide−organosilicate hybrid films (PI + ABA-POSS 2 wt %). Scale bars: (a) 500 and (b) 200 nm. (c) TGA thermograms of polyimide and its hybrid films. Unit of POSS content is wt %.

Morphology and Physical Properties of Polyimide−Organosilicate Composite Materials. According to SEM images of the film surface (Figure 4a) and cross-section (Figure 4b), there are no clear vestiges of silicates typically observed in composite materials.[25,30,33] The fractured image (Figure 4b) looks almost identical to pure BTDA-*m*-BAPS. It is assumed that ABA-POSSs are well dispersed in the polyimide matrix by compatible amine functional groups. Figure 4c shows changes in thermal decomposition in a pure polyimide reference material and the other hybrid polyimides. Generally, thermal stability is enhanced in hybrid films. The actual values of 1% weight loss temperature, $T_{wl1\%}$, are shown in Table 1. As seen in the data, the addition of silicates increased the weight loss temperature, more substantially in POSS with amino-functional groups. This result is in accord with previous reports.[26,32] Notably, 1 wt % of commercial POSS contains a larger mole number than that of ABA-POSS, considering its molecular weight. However, 1% octa-amino POSS and 1% ABA-POSS gave an almost identical increase of thermal stability. Also, the solvent resistivity of polyimide was improved similarly in both hybrid films. The slight dissolving behavior of polyimide with 1% POSS in DMF and DMAc was not observed in the amino-functional POSS containing films. Probably, the comparable effect of octa-amino POSS and the less functional group of ABA-POSS may come from the fact that all eight functional amines are not linked directly to polyimide chains because of its steric hindrances.

One of the most critical requirements of plastic substrates, their visible and near UV light transmittance (Tr), were evaluated (Figure 5a). Tr results and haziness are listed in Table 1. They show marked improvements in Tr in the case of hybrid films, especially in the visible light region, 450−700 nm. This is not surprising because POSS-like materials generally show higher visible light transmittance than organic polymers.[38,39] Notably, lower refractive index of POSS than polymer matrix can disturb visible light transmission in the composites. This provides lower Tr of nonfunctionalized POSS system than the case of amine-functionalized POSSs those have chemical bonds with polyimide chains. However, the Tr for 1% octa-amino POSS is a little lower, and it is well recognized in the near UV light region (arrow in Figure 5a). The energy involved in charge transfer between electron donor (nitrogen) and acceptor (carbonyl group) in polyimides corresponds to the wavelength of near UV light.[17] Therefore, the strong absorption of violet light makes one see polyimide films as yellowish. In the case of octa-amino POSS, which show higher Tr in wavelength longer than 500 nm, a large number of imide bonds and presumably the remaining amine groups may contribute to lower transmittance in 400 nm wavelength region. In contrast, ABA-POSS added films show improved properties

Table 1. Optical, Thermal, And Mechanical Properties of Polyimide−Organosilicate Hybrid Films[a]

films	$T_{\mathrm{wl1\%}}$ (°C)	Tr (%)[b]	haziness	CTE (ppm/°C)	tensile modulus (GPa)	maximum strain (%)
polyimide (PI)	370 ± 5	86.1 ± 0.5	0.9 ± 0.1	51.0 ± 2.4	2.54 ± 0.08	15.5 ± 1.8
PI + POSS 1%	389 ± 3	88.2 ± 0.4	4.5 ± 0.2	47.5 ± 1.6	2.85 ± 0.17	9.5 ± 0.9
PI + octa-amino POSS 1%	394 ± 3	86.4 ± 0.3	3.9 ± 0.3	44.2 ± 2.6	3.26 ± 0.24	12.6 ± 1.5
PI + ABA-POSS 1%	395 ± 5	91.7 ± 0.3	1.4 ± 0.1	42.1 ± 1.7	3.07 ± 0.19	13.4 ± 1.7
PI + ABA-POSS 2%	405 ± 4	90.8 ± 0.6	1.6 ± 0.2	40.2 ± 1.3	3.24 ± 0.22	9.3 ± 1.1

[a] Data are reported with the standard uncertainty. [b] Transmittance of visible light, wavelength between 400 and 700 nm.

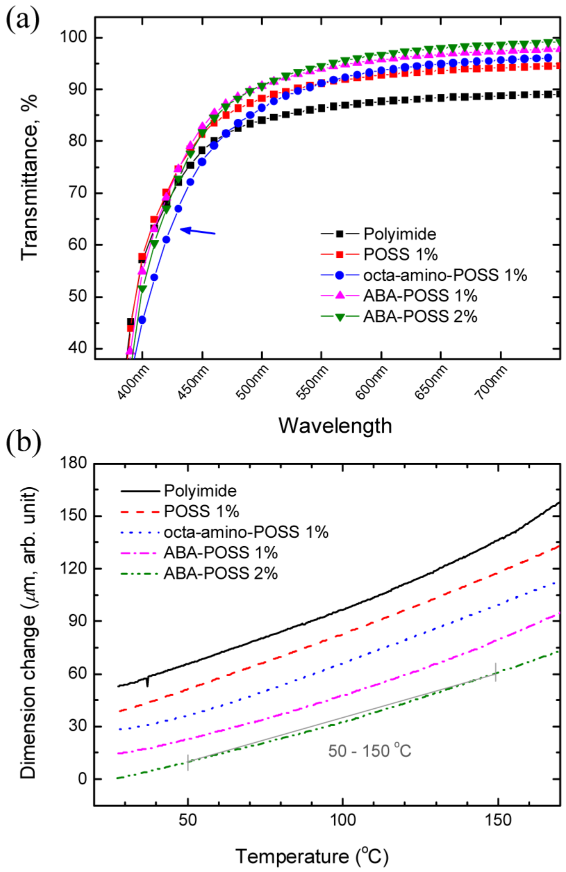


Figure 5. (a) Transmittance of polyimide−organosilicate hybrid films as a function of wavelength. (b) Dimension changes in TMA scanning. TMA data are off set for clarity.

both in Tr without large sacrifice in 400 nm region and haziness, compared to hybrid films with nonfunctional POSS.

Another critical requirement of dimensional stabilities as a function of temperature were also measured (Figure 5b). Considering the use of plastic substrates in display devices, CTEs as low as those of glass substrates are essential, because thermal expansion mismatch between the substrates and the circuits on them often leads to warpage problems.[9,10,56] CTEs calculated from the film's dimension change during thermal ramping from 50 to 200 °C are shown in Table 1. TMA thermograms showed slight inflections around the glass transition of the materials, 250−280 °C. With amine-functionalized POSS insertion, T_g was slightly increased, with providing highly brittleness in case of octa-amino POSS due to the cross-linking density. T_g values obtained from DSC measurements are shown in S3 in the Supporting Information. With the increase in POSS content, CTE decreased up to ~20% from the value of reference polyimide. Among polyimide−organosilicate hybrid films, POSSs with amino-functional groups play more positive role in reducing CTE. That may be due to the cross-linking achieved between polyimide chains and amine functionalized POSS. According to previous studies,[20,37,57] closed packing and increased density induced by thermal annealing in polyimide films provide CTE increments. This indicates stronger chemical interaction between the polymer chains, such as cross-linking, can provide decreased CTEs. Also, ABA-POSS containing films show substantially lower CTE than the case of single cage structured POSS. CTE depends critically on molecular bond structures, such as monomer rigidity and end group mobility. In a polyimide matrix, POSS with amino-function groups could be well dispersed. This indicates the alkyl bridge between POSSs plays a different role in thermal expansion from when they are aggregated alone. It is supposed that the alkyl bridge in BTSE reduced the number of mobile end groups, such as methyl, and decreased CTE was obtained. This confirms that CTE variation should be first explained with respect to molecular basis.

Optical properties (Tr, haziness) and thermal stabilities (T_{wl} and CTE) in Table 1 are the most importantly required properties for the plastic display substrates. Current glass substrates has Tr of higher than ~92% and haziness is lower than 1.0. In addition, there is no weight loss during thermal process and CTE of ~9 ppm/°C.[1−7] In this regard, current properties of plastic materials, including the new composite films, are still far from the full applications as the substrates, even though their merits include flexibility.[8−12] Among the popular display devices, only E-paper, small-sized OLED, and low-performance LCD can be manufactured with plastic substrates. Flexibility as well as low density is a key advantage of plastic substrates. For the quantification of flexibility, we measured modulus and strain of the films. BTDA is a rigid molecule and has low reactivity with anhydride. This causes the polyimide to have a low molecular weight and the films to have relatively lower maximum strain compared to other polyimides,[58] in spite of the flexible nature of *m*-BAPS. Generally, the addition of silicates into polymer backbones gives increase in tensile modulus and reduction in elongation to break that is closely related to film brittleness. Polyimide-organosilicate hybrid films, accordingly, show up to ~30% increase in tensile modulus but decreased elongation to break (Table 1). This indicates that developing flexible substrate materials by the insertion of organosilicates requires the balancing of improved optical and thermal properties against the elongation properties.

■ CONCLUSIONS

Through hydrolysis and polycondensation, a new type of organosilicate for polyimide composites was prepared. In order to improve thermo-dimensional stability and miscibility of the organosilicate in polymer chains, alkyl chain bridges and amine functional groups were introduced, respectively. Finally, polyimide−organosilicate hybrid films were fabricated through further condensation and imidization of the organosilicate with polyimide precursors. Characterizations of the thermomechanical properties confirmed that thermal expansion primarily originates from molecular bond structures and end groups of the molecules. Properties of the new composite films still need enhances specifically in their thermo-dimensional stability for the applications in display devices. The results also suggested a trade-off in developing plastic substrates, namely, improving optical and thermal properties without compromising elongation properties in the hybrid films.

■ ASSOCIATED CONTENT

Supporting Information

Additional figures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

PSSQ, polysilsesquioxanes
POSS, polyhedral oligomeric silsesquioxane
CT, charge transfer
ABA-POSS, alkyl chain bridged amino-polyhedral oligomeric silsesquioxane
MTMS, methyl(trimethoxy)silane
BTSE, bis(triethoxysilylethane)
APhTMS, aminophenyl(trimethoxy)-silane
T_8, cage structured POSS
PAA, poly(amic acid)
PI, polyimide
BTDA, bicyclo-[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride
m-BAPS, 2,2-bis[4-(3-aminophenoxy) benzene]
DMAc, Dimethyl acetamide
GPC, gel permeation chromatography
MALDI-TOF-MS, matrix-assisted laser desorption/ionization time-of-flight mass spectrometry
T_g, glass transition temperature
CTE, coefficient of thermal expansion
Tr, transmittance
$T_{wl1\%}$, temperature of 1% weight loss

■ REFERENCES

(1) Lewis, j. *Materialstoday* **2006**, *9*, 38−45.
(2) Hellemans, A. *IEEE Spectrum* **2000**, *37*, 18−21.
(3) Ong, B. *Laser Focus World* **2004**, *40*, 85−88.
(4) Savage, N. *Laser Focus World* **1999**, *35*, 42−46.
(5) Hogan, H. *Photon. Spectra* **2003**, *37*, 66−72.
(6) Jazi, A. Y.; Yoon, S.; Liu, J. J. *Ind. Eng. Chem. Res.* **2012**, *51*, 10887−10894.
(7) McAlpine, M. C.; Friedman, R. S.; Lin, S. J. K.-h.; Wang, W. U.; Lieber, C. M. *Nano Lett.* **2003**, *3*, 1531−1535.
(8) Sulaiman, S.; Brick, C. M.; De Sana, C. M.; Katzenstein, J. M.; Laine, R. M.; Basheer, R. A. *Macromolecules* **2006**, *39*, 5167−5169.
(9) Okura, J. H.; Shetty, S.; Ramakrishnan, B.; Dasgupta, A.; Caers, J. F. J. M.; Reinikainen, T. *Microelectron. Reliab.* **2000**, *40*, 1173−1180.
(10) Nysaether, J. B.; Lundstrom, P.; Liu. *J. IEEE Trans. Packag., Manuf. Technol., Part A* **1998**, *21*, 281−287.
(11) Jang, J. *Mater. Today* **2006**, *9*, 46−52.
(12) MacDonald, W. A. *J. Mater. Chem.* **2004**, *14*, 4−10.
(13) Bessonov, M. I.; Zubkov, V. A. *Polyamic Acids and Polyimides: Synthesis, Transformations, and Structure*; CRC Press: Boca Raton, FL. 1993; Chapter 1−3, pp 3−198.
(14) Wilson, D.; Stenzenberger, H. D.; Hergenrother, P. M. *Polyimides*; Chapman and Hall: New York, 1990; Chapter 3, pp 126−183.
(15) Mulliken, R. S. *J. Am. Chem. Soc.* **1952**, *74*, 811−824.
(16) Yan, J.; Wang, Z.; Gao, L.; Ding, M. *Macromolecules* **2004**, *39*, 7555−7560.
(17) Hasegawa, M.; Horie, K. *Prog. Polym. Sci.* **2001**, *26*, 259−335.
(18) Simone, C. D.; Auman, B. C.; Carcia, P. F.; Wessel, R. A. *Low color polyimide compositions useful in optical type applications and methods and compositions relating thereto*. U.S. patent 7 550 194, Aug 3, 2005.
(19) Feiring, A. E.; Auman, B. C.; Wonchoba, E. R. *Macromolecules* **1993**, *26*, 2779−2784.
(20) Liou, H.-C.; Ho, P. S.; Tung, B. *J. Appl. Polym. Sci.* **1998**, *70*, 261−272.
(21) Maruo, Y. Y.; Andoh, Y.; Sasaki, S. *J. Vac. Sci. Technol. A* **1993**, *11*, 2590−2596.
(22) Calia, M.; Monte, D.; Serra, A.; Mantecon, A.; Cadiz, V. *J. Appl. Polym. Sci.* **1996**, *60*, 2177−2183.
(23) Okada, A.; Usuki, A. *Macromol. Mater. Eng.* **2006**, *291*, 1449−1476.
(24) Li, T.-L.; Hsu, S. L.-C. *J. Phys. Chem. B* **2010**, *114*, 6825−6829.
(25) Wang, S.; Ahmad, Z.; Mark, J. E. *Chem. Mater.* **1994**, *6*, 943−946.
(26) Tamaki, R.; Choi, J.; Laine, R. M. *Chem. Mater.* **2003**, *15*, 793−797.
(27) Wright, M. E.; Petteys, B. J.; Guenthner, A. J.; Fallis, S.; Yandek, G. R.; Tomczak, S. J.; Minton, T. K.; Brunsvold, A. *Macromolecules* **2006**, *39*, 4710−4718.
(28) Son, M.; Han, S.; Han, D.; Kim, Y.; Kim, J.; Kim, Y.; Ha, C.-S. *Polym. Bull.* **2008**, *60*, 713−723.
(29) Scott, D. W. *J. Am. Chem. Soc.* **1946**, *68*, 356−358.
(30) Baney, R. H.; Itoh, M.; Sakakibara, A.; Suzuki, T. *Chem. Rev.* **1995**, *95*, 1409−1430.
(31) Liu, H.-S.; Jeng, S.-C. *Opt. Mater.* **2013**, *35*, 1418−1421.
(32) Choi, J.; Tamaki, R.; Kim, S. G.; Laine, R. M. *Chem. Mater.* **2003**, *15*, 3365−3375.
(33) Ahmad, Z.; Mark, J. E. *Chem. Mater.* **2001**, *13*, 3320−3330.
(34) Rodriguez-fernandez, O. S.; Gilbert, M. *J. Appl. Polym. Sci.* **1997**, *66*, 2121−2128.
(35) Chen, Y.; Iroh, O. *Chem. Mater.* **1999**, *11*, 1218−1222.
(36) Jung, Y.; Kline, R. J.; Fischer, D. A.; Lin, E. K.; Heeney, M.; McCulloch, I.; DeLongchamp, D. A. *Adv. Funct. Mater.* **2008**, *18*, 742−750.
(37) Jung, Y.; Yang, Y.; Kim, S.; Kim, H.-S.; Park, T.; Yoo, B. W. *Eur. Polym. J.* **2013**, *49*, 3642−3650.
(38) Kickelbick, G. *Hybrid Materials. Synthesis, Characterization, And Application*; Wiley-VCH Verlag: Weinheim, Germany, 2007; Chapter 6, pp 225−254.
(39) Gómez-Romero, P.; Sanchez, C. *Functional Hybrid Materials*; Wiley-VCH Verlag: Weinheim, Germany, 2004; Chapter 3, pp 50−85.
(40) Kim, H.-J.; Lee, J.-K.; Kim, J. B.; Park, E. S. *J. Am. Chem. Soc.* **2001**, *123*, 12121−12122.

(41) Park, E. S. *Synthesis, Structure and Properties of Polysilsesquioxanes*. Ph.D. thesis, Seoul National University, Seoul, Korea, 2008.

(42) Yang, S.; Pai, J. C.-H.; Pai, C.-S.; Dabbagh, G.; Nalamasu, O.; Reichmanis, E.; Seputro, J.; Obeng, Y. S. *J. Vac. Sci. Technol. B* **2001**, *19*, 2155−2161.

(43) Duchateau, R. *Chem. Rev.* **2002**, *102*, 3525−3542.

(44) Laine, R. M. *J. Mater. Chem.* **2005**, *15*, 3725−3744.

(45) Gilman, J. W.; Schlitzere, D. S.; Lichtenhan, J. D. *J. Appl. Poylm Sci.* **1996**, *60*, 591−596.

(46) Baney, R. H.; Itoh, M.; Sakakibara, A.; Suzuki, T. *Chem. Rev.* **1995**, *95*, 1409−1430.

(47) Samthong, C.; Laine, R. M.; Somwangthanaroj, A. *J. Appl. Polym. Sci.* **2013**, *130*, 3601−3608.

(48) Kannan, R. Y.; Salacinski, H. J.; Butlerand, P. E.; Seifalian, A. M. *Acc. Chem. Res.* **2005**, *38*, 879−884.

(49) Fan, H.; Hartshorn, C.; Buchheit, T.; Tallant, D.; Assink, R.; Simpson, R.; Kissel, D. J.; Lacks, D. J.; Torquato, S.; Brinker, C. J. *Nat. Mater.* **2007**, *6*, 418−423.

(50) Ro, H. W.; Char, K.; Jeon, E.; Kim, H.-J.; Kwon, D.; Lee, H.-J.; Lee, J.-K.; Rhee, H.-W.; Soles, C. L.; Yoon, D. Y. *Adv. Mater.* **2007**, *19*, 705−710.

(51) Huang, J.-C.; Zhu, Z.-K.; Yin, J.; Zhang, D.-M.; Qian, X.-F. *J. Appl. Polym. Sci.* **2001**, *79*, 794−800.

(52) Park, E. S.; Ro, H. W.; Nguyen, C. V.; Jaffe, R. L.; Yoon, D. Y. *Chem. Mater.* **2008**, *20*, 1548−1554.

(53) Brintzinger, H. H.; Fischer, K.; Mülhaupt, R.; Rieger, B.; Waymouth, R. *Angew. Chem., Int. Ed. Engl.* **1995**, *107*, 1255−1283.

(54) Afarinkia, K.; Vinader, V.; Nelson, T. D.; Posner, G. H. *Tetrahedron* **1992**, *48*, 9111−9171.

(55) Komatsu, K.; Nishinaga, T. *Synlett* **2005**, *2*, 187−202.

(56) Leterrier, Y.; Medico, L.; Demarco, E.; Manson, J.-A. E.; Betz, U.; Escola, M. F.; Olsson, M. K.; Atammy, F. *Thin Solid Films* **2004**, *460*, 156−166.

(57) Liou, H.-C.; Ho, P. S.; Stierman, R. *Thin Solid Films* **1999**, *339*, 68−73.

(58) Agag, T.; Koga, T.; Takeichi, T. *Polymer* **2001**, *42*, 3399−3408.