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A series of cationically photopolymerizable inorganic-organic hybrid epoxy-functionalized thermoplastic polysilsesquioxanes were synthesized and their thermal, mechanical, optical, and barrier properties investigated.

LPPGSQ

UV-Cure

LPPCESQ

UV-Cure

High Barrier to Oxygen & Water Vapor!!!
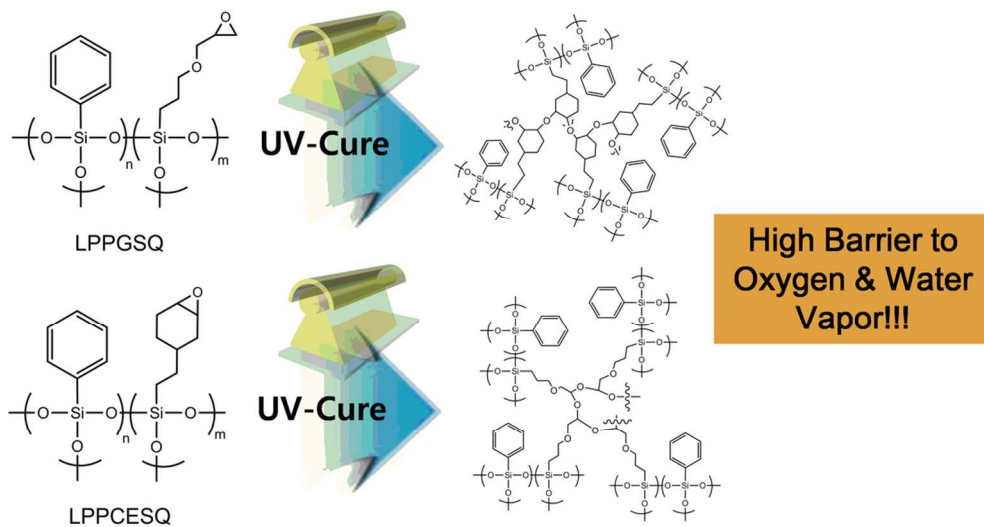
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Journal Name

ARTICLE

Cationically Photopolymerizable Epoxy-Functionalized Thermoplastic Polysilsesquioxanes: Synthesis and Properties

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A series of epoxy-functionalized inorganic-organic hybrid ladder-like strictured polysilsesquioxanes were synthesized in one-batch via a base-catalyzed co-solvent system. Two types of epoxy functionalities were examined: aliphatic and cycloaliphatic. Obtained polymeric epoxy-functionalized ladder-like polysilsesquioxanes were cationically photopolymerized under UV irradiation over glass and plastic substrates. Obtained cross-linked films were examined as hardcoating materials as their thermal, optical, mechanical, and barrier properties were studied. These materials showed superior thermal properties (Td > 400 $^{\circ}$C), high optical transparency (> 95%), high pencil hardness (4H-9H), low dielectric constant (3.0-3.6), and good barrier properties (WVTR < 10^1 g/m2day/atm, OTR < 10^2 g/m2day/atm).

Introduction

Photocurable polymers have been extensively investigated for their various advantages over conventional water and solvent-based thermal curing processes.[1,2] Such advantages include increased curing speeds, low cost, low processing temperature, and low energy consumption.[3,4] These properties have rendered these materials applicable for a variety of applications such as optical hardcoats for lenses and plastic surfaces[5-7], LED packaging materials[8], gate dielectrics[9], and nano-imprint lithography.[10-11] Compared with small molecule or oligomeric photocurable moieties, photocurable polymers exhibit low shrinkage, enhanced thermal stability, and low volatility.[11]

Photocurable functionalities can be divided into three main classes: acryl, thiol-ene, and epoxy. While acryl-based formulations are known for their fast polymerization rates and high crosslinking density[7], attributed to the free radical mechanism by which they are cured, acryl formations show relatively poor adhesion to plastic surfaces, and are sensitive to oxygen and moisture. Thiol-ene curable hybrids are another unique class of photocurable formulations in which the thiol proton is initiated via UV and cured with unsaturated vinyl or acryl-based resins.[12,13] While thiol-ene curable formulations do not suffer from oxygen inhibition and are cured extremely fast[14] compared with purely acryl-based formations, the thermal stability of the thiol groups, as well as the distinct putrid odor of the thiol compounds have rendered these formations unsuitable for industrial commercialization. The third class of photocurable functional groups are epoxy-functionalized hybrids, which are especially attractive for industrial use and the more ubiquitous epoxy-amine thermal curing formulations have

been rigorously studied previously.[15] Epoxy groups may also be cationically photopolymerizable using photoacid generating catalysts.[16] While the crosslinking speed has been known to be lower than conventional acryl or thiol-ene formulations, the living polymerization nature of these curing systems have been useful for the tuning of optical and mechanical properties.

Epoxy groups can also be classified by their structure: aliphatic and cycloaliphatic. While all epoxies are linked through aliphatic carbon groups, cycloaliphatic epoxies are linked with cyclohexyl groups, substantially hindering the adjacent carbons for ring opening polymerizations. As such, cycloaliphatic epoxies exhibit lower curing speeds when compared to aliphatic epoxies. However, cycloaliphatic epoxies exhibit significantly improved thermal stability over aliphatic epoxies due to the cyclohexyl groups, which is of critical importance in applications in electronic devices to prevent yellowishness. Also, hybrid cycloaliphatic resins have been reported to have enhanced thermo-mechanical properties over methacryl-based resins.[17]

Despite the advantages of the rigorously studied organic polymers of various functionalities discussed above, the organic polymers are limited by their low thermal stability and low resistance to yellowishness arising from the oxidative degradation of the hydrocarbon backbones initiated between free radicals generated from the catalyst and/or oxygen in air.[18] Therefore many researchers have investigated inorganic-organic hybrid materials due to their thermal and mechanical stability.

Polysilsesquioxanes, of chemical formula [RSiO1.5]n, are inorganic-organic hybrid materials synthesized by sol-gel

reactions of tri-functional silanes.[19] Of the three structural classes of polysilsesquioxanes: resins, POSS, and ladder-like, ladder-like polysilsesquioxanes (LPSQs) are a unique structural class of organic-inorganic hybrid materials in which the Si-O-Si bonds comprise a fully condensed, double-stranded ladder and the organic functional groups pendant to the siloxane bonds.[20-22] In addition to the superior thermal properties[22] of LPSQs over POSS and incompletely condensed resins, LPSQs have high molecular weight and contain insignificant amounts of uncondensed silanol groups[21], eliminating the need for high temperature curing process to cure the uncondensed silanol groups.

In this study, a series of aliphatic and cycloaliphatic hybrid ladder-like structured polysilsesquioxanes were synthesized, characterized, and their various thermal, mechanical, optical, and barrier properties examined. By examining the effect on epoxy-structure to the various properties investigated, insights into the design of highly applicable materials were elucidated.

Experimental

Materials

Phenyltrimethoxysilane (Shin Etsu, 98%), 3-glycidoxypropyltrimethoxy (Shin Etsu, 98%), [2-(3,4-epoxycyclohexyl)ethyl]trimethoxysilane (Shin Etsu, 98%), and THF (J.T. Baker) were vacuum distilled over calcium hydride before use. Potassium carbonate (Dae Jung) was dried in the vacuum oven at 40°C overnight before use. Photoinitiator Igracure 250 (BASF) was used as received. All other solvents (J.T. Baker) were used as received. PET substrates were graciously donated by Dongjin Semichem Co.

Typical synthesis of ladder-like structured poly(phenyl-co-glycidoxypropyl)silsesquioxanes (LPPGSQ)

Synthesis of LPPGSQ64, with phenyl:glycidoxypropyl ratio 6:4, was conducted following a modified literature procedure as shown in Scheme 1.[22] Typically, in a 100ml round bottom flask, a transparent mixture of potassium carbonate (0.04g, 0.29mmol), deionized water (4.8ml, 0.267 mol), and THF (18ml) was prepared. To this solution, a monomer mixture of phenyltrimethoxysilane (9.52g, 0.48mol) and 3-glycidoxypropyltrimethoxysilane (7.95g, 0.32mol) was added dropwise under N_2. The reaction mixture was stirred vigorously for five days at room temperature, or until the molecular weight reached its maximum. After evaporation of the volatiles, the white resinous portion was dissolved in 100ml dichloromethane and extracted with water three times. After collection of the organic portions, drying with anhydrous magnesium sulfate, filtering, and evaporation of dichloromethane, LPPGSQ64 was obtained as a white powder (13.3g, 95% yield). ^{1}H NMR ($CDCl_3$, ppm): 0.35-0.75 (t, Si(CH_2CH$_2$CH$_2$OCH$_2$CHOCH$_2$, 2H), 1.3-1.7 (m, Si(CH$_2$$CH_2CH_2OCH_2$CHOCH$_2$, 1H), 2.5-2.7 (d, Si(CH$_2CH_2CH_2OCH_2$$CHOCH_2$, 1H), 2.8-3.0 (m, Si(CH$_2CH_2CH_2OCH_2$CHOC$H_2$, 2H), 3.0-3.3 (m, Si(CH$_2CH_2CH_2OCH_2$CHOCH$_2$, 2H), 3.2-3.4 (m,

Si(CH$_2$CH$_2$CH$_2$OCH_2CHOCH$_2$, 2H), 7.2-8.0 (m, Si(C_6H_5), 5H), ^{29}Si NMR (ppm): -64~-70 ppm, , -77~-82 ppm.

Characterization

Number average molecular weight (M_n) and molecular weight distributions (M_w/M_n) of the polymers were measured by JASCO PU-2080 plus SEC system equipped with refractive index detector (RI-2031 plus), UV detector (λ=254 nm, UV-2075 plus), and Viscotek SLS apparatus using THF as the mobile phase at 40°C with a flow rate of 1 mL/min. The samples were separated through four columns (Shodex-GPC KF-802, KF-803, KF-804, KF-805). ^{1}H-NMR, ^{29}Si NMR spectra were recorded in $CDCl_3$ at 25 °C on a Varian Unity INOVA ([1]H: 300 MHz, [29]Si: 59.6MHz). FT-IR spectra were measured using Perkin-Elmer FT-IR system (Spectrum-GX) using solvent cast films on KBr pellets. Thermal gravimetric analysis (TGA) was performed by TA Instrument TGA 2950 under N_2. UV-Vis Spectroscopy was conducted on a HP 8452A Diode Array Instrument. Refractive Indices were measured using an Abbe Refractometer. Pencil hardness tests were conducted using standard ASTM D 3363-92a and ECCA T4 testing methods on a Gardco/Wolff Wilborn instrument with a fixed pressure of 7.5 N at an angle of 45°. WVTR and OTR measurements were conducted on a MOCON W-model 3/33 and MOCON OX-TRAN 2/21 tester, respectively.

Film Fabrication

LPSQ samples were dissolved in MIBK (40 wt%) with a 3 wt% content of photoinitiator Igracure 250 with respect to the LPSQ compound. Afterwards, these solutions were shaken and sonicated for one hour until a transparent, viscous solution was prepared. Afterwards, these solutions were cast on a precleaned glass slide or PET substrates and scraped using a Dr. Blade preset at 20μm. Fabricated films were left at room temperature overnight and further dried in a vacuum oven at 40 °C for 2hr. Film thicknesses were measured using a micrometer. LPSQ coated PET or Glass Slides were then irradiated with a HITACHI UV-lamp system with a lamp intensity of 100 mW/cm², with a total UV energy output of 3 J/cm². Free standing films were obtained by lifting off the photocured films casted on non-sticking PTFE films.

Results and Discussion

The synthesis of aliphatic and cycloaliphatic epoxy-functionalized ladder-like structured poly(phenyl-co-glycidoxypropyl)silsesquioxane (LPPGSQ) and poly(phenyl-co-cyclohexylepoxyethyl)silsesquioxane (LPPCESQ) followed a modified literature procedure[21,22] in which a monomer mixture solution of phenyltrimethoxysilane and epoxy-functionalized trimethoxysilane were hydrolyzed and condensed in a base-catalyzed sol-gel reaction (Scheme 1). This method has been highly effective to obtain fully condensed, high molecular weight polysilsesquioxanes of various homopolymers and copolymers with various organic copolymer compositions.[22] In designing LPPGSQ and LPPCESQ, the

epoxy-functionalized polysilsesquioxanes were copolymerized with phenyl moieties for thermal stability, refractive index control, and film robustness. It is noteworthy to add that these random copolymers do not show a particular repeating unit sequence, but are highly amorphous polymers. The obtained epoxy-functionalized polysilsesquioxanes were photocured (Scheme 2) to give highly crosslinked structures.
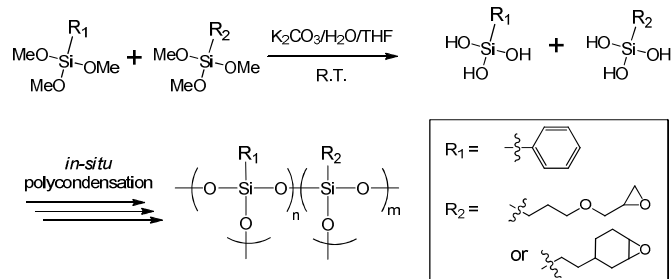
Scheme 1 Synthesis of LPPGSQ and LPPCESQ compounds
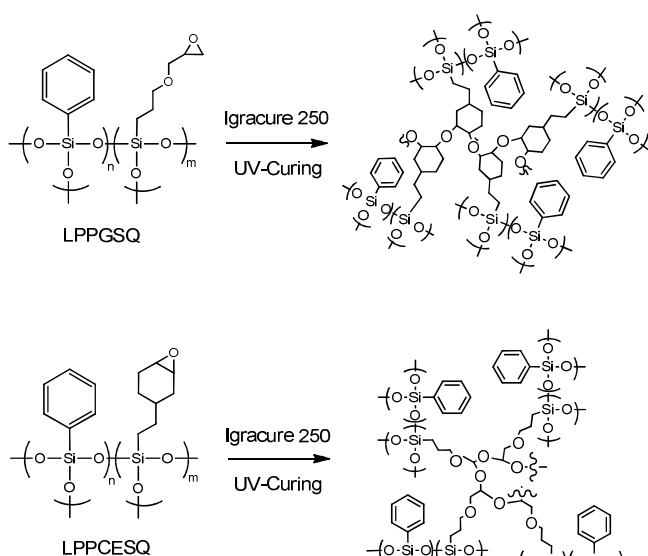
Scheme 2 Photocuring Processes of LPPGSQ and LPPCESQ compounds

Obtained epoxy-functionalized LPPGSQ and LPPCESQ series were first characterized using ^{1}H NMR as shown in Fig. 1. As shown, both LPPGSQ and LPPCESQ series were fully hydrolyzed and condensed as no methoxy groups at 3.55 ppm and no silanol groups at 5.0 ppm were found. The integrated peaks assigned to the glycidoxypropyl and cyclohexylethyl groups relative to the phenyl groups confirmed the initial monomer feed ratio. Moreover, the broad peaks of the aromatic and aliphatic protons were indicative of high molecular weight as confirmed via GPC analyses.
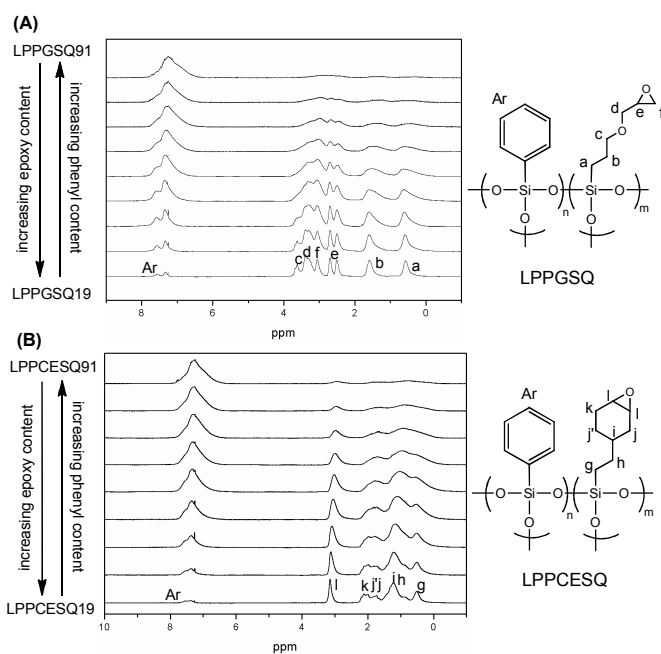

Fig. 1 ^{1}H NMR spectra for (A) LPPGSQ series and (B) LPPCESQ series

LPPGSQ and LPPCESQ were further characterized with FT-IR. Fig. 2 shows the characteristic peaks for the LPSQs, as the sharp and high intensity bimodal siloxane absorption bands at 1150 cm^{-1} and 1040 cm^{-1}, assigned to the horizontal and vertical Si-O-Si modes. Also, as expected, the intensity of the peaks for phenyl groups at 1451 cm^{-1} and 1600 cm^{-1} increased with increasing phenyl content, ie) LPPGSQ19 → LPPGSQ91. Also, the peaks for the aliphatic epoxy groups (denoted AE in Fig. 2) were found at 910 cm^{-1}, and the cyclohexylepoxy (denoted CE in Fig. 2) were found at 793 cm^{-1}, as previously reported.[22]
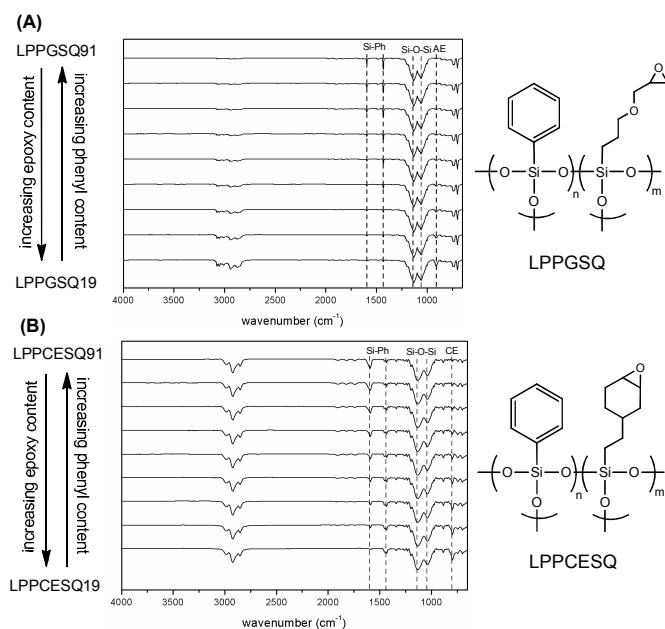

Fig. 2 FTIR spectra for (A) LPPGSQ series and (B) LPPCESQ series

The siloxane structure and degree of condensation were analyzed by ^{29}Si NMR (Fig. 3). For polysilsesquioxanes, the characteristics peaks of T^3 (Ph-Si(OSi-)$_3$) and T^2 (Ph-Si(OSi-)$_2$OH) structures are centered at -77 and -70 ppm respectively, and the T^3 (alkyl-Si(OSi-)$_3$) and T^2 (alkyl-Si(OSi-)$_2$OH) for the cycloaliphatic epoxy-Si structures are centered at -68 and -58 ppm respectively.[22] As shown in Fig. 3, only the T^3 peaks of (Ph-Si(OSi-)$_3$) and (alkyl-Si(OSi-)$_3$) are shown as *a* and *b*, indicating that the siloxane structures were fully condensed. Moreover, the integrated ratio between T^3 of (Ph-Si(OSi-)$_3$) and T^3 (alkyl-Si(OSi-)$_3$) reflected the initial copolymerization molar feed ratio. Also, the half-maximum width ($\Delta_{1/2}$) is a common indicator of ladder-like and perfect ladder Si-O-Si structures.[20,23] The epoxy-functionalized polysilsesquioxanes obtained in this study showed a $\Delta_{1/2}$ of 227 Hz for the Si-Phenyl and 298 Hz for the Si-Epoxy groups. As these values are larger than for previous reports, which gave $\Delta_{1/2}$ of 149 Hz for the polyphenylsilsesquioxane synthesized by Zhang,[20] and $\Delta_{1/2}$ of 118 Hz for the polymethylsilsesquioxane synthesized by Gunji,[23] the epoxy-functionalized polysilsesquioxanes synthesized in this study probably have a significant amount of irregular structures.
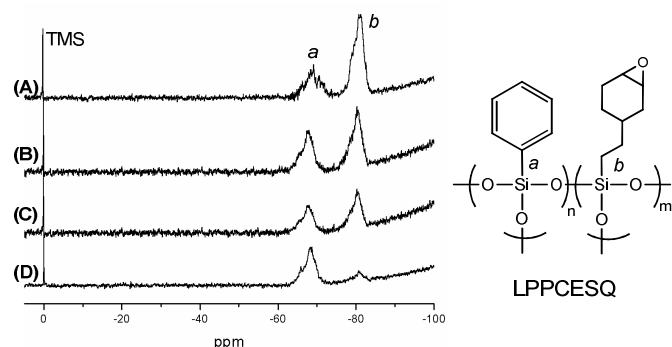

Fig. 3 ^{29}Si NMR spectra for (A) LPPCESQ28 (B) LPPCESQ46 (C) LPPCESQ64 (D) LPPCESQ82

The photocuring rates of representative aliphatic epoxy-functionalized LPPGSQ64 and cycloaliphatic epoxy-functionalized LPPCESQ64 were analyzed with FT-IR (Fig. 4). The aliphatic and cycloaliphatic epoxy conversion as function of irradiation time (Fig. 4A and 4B insets) showed a linear rise in epoxy conversion calculated from the relative depreciation of the FT-IR absorption peak integrative ratio assigned to the aliphatic and cycloaliphatic epoxy group at 910 cm^{-1} and 793 cm^{-1}, respectively. This linear increase in conversion was indicative of living polymerization conversions. However a significant difference between the photocuring rates was observed between the LPPGSQ and LPPCESQ series, as the LPPGSQ series were found to have a faster conversion,[24] as LPPGSQ showed a conversion of 80% at 133 sec, while LPPCESQ showed a conversion of 86% at 200 sec. Also, noteworthy is that no significant amounts of hydroxyl groups were detected at various curing rates. While epoxy-ring opening reactions are bound to form hydroxyl groups which may also self-condensed to form water molecules, the

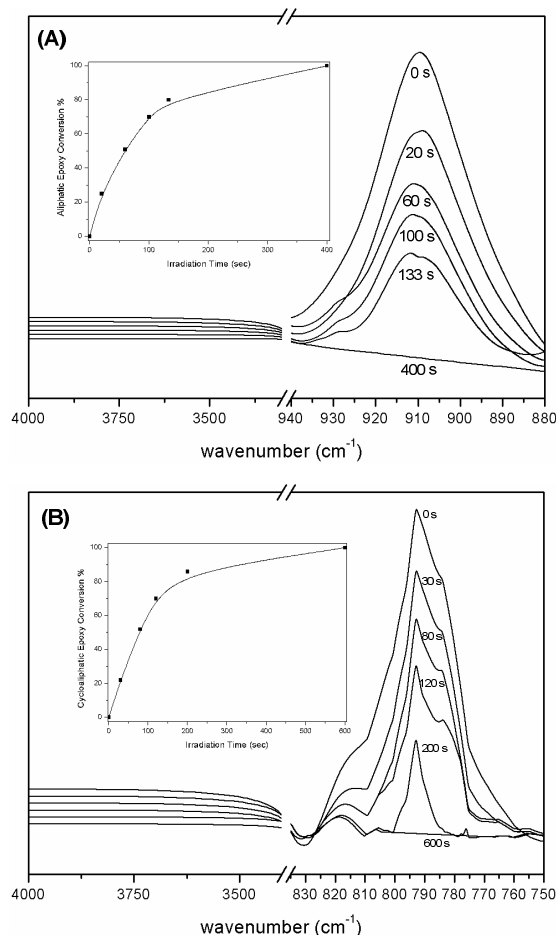photocuring reactions of LPPGSQ and LPPCESQ were found form almost undetectable hydroxyl groups at 3500 cm^{-1}.

Fig. 4 FTIR spectra of (A) LPPGSQ64 Aliphatic Epoxy Photo-conversion Rates and (B) LPPCESQ64 Cycloaliphatic Epoxy Photo-conversion Rates

The various thermal, mechanical, and optical properties of photopolymerized epoxy-functionalized polysilsesquioxanes are shown in Table 1 and Table 2. The obtained epoxy-functionalized polysilsesquioxanes were of high molecular weight (>10 k), with thermoplastic behavior, as evident from the non-detection of uncondensed silanols showing characteristic weight loss at 150 $^{\circ}$C. In comparing the thermal stability of the LPPGSQ and LPPCESQ series, the LPPCESQ series showed slightly higher thermal stability, attributed to the more stable cyclohexyl groups. Also, the photocured films coated on glass and PET are shown. All of the LPPGSQ and LPPCESQ series exhibited superior mechanical and scratch-resistant properties as indicated by high pencil hardness values, regardless of glass or plastic substrates, with a high pencil hardness of 9H, even on PET substrates. In most cases, the pencil hardness values of hardcoatings on plastics are exceeding lower relative to the values shown on glass or Si substrates, due to the low adhesion and surface abrasion arising to the difference in surface energy between the coating and substrate layers.[5] It is interesting to note that the pencil hardness values increase with increase in relative phenyl

content, but decreases after a certain point. This tendency holds true for both LPPGSQ and LPPCESQ series in thin film, as a phenyl/epoxy ratio of 6:4 gave the largest surface moduli (> 8 GPa) This can be explained by two reasons: first, a phenyl/epoxy ratio of 6:4 gives a polymer with the largest molecular weight, and second, the phenyl/epoxy ratio of 6:4 seems to be the optimal phenyl content to give robustness, and enough epoxy content to easily cure the polymer. Moreover, the refractive indices and % transmittance values are tabulated. As expected, the refractive indices of LPPGSQ increased with increasing phenyl content, and the photocured films were highly transparent. The refractive indices of the LPPGSQ series were slightly higher than those of LPPCESQ, which can be attributed to the additional oxygen atom increasing the overall polarity of the film.

Table 1. Mw, PDI, Thermal, and Mechanical Properties of LPPGSQ Hybrids

Sample Code	Mw[a] (g/mol)	PDI[b]	T_d(°C)[c]	Pencil Hardness on glass/PET	Surface Modulus (GPa)	Refractive Index	% Transmittance @ 450nm[d]
LPPGSQ19	12k	2.4	382	3H/3H	5.4	1.444	96
LPPGSQ28	14k	2.9	388	4H/4H	5.4	1.457	96
LPPGSQ37	18k	2.7	389	5H/4H	5.9	1.470	95
LPPGSQ46	21k	3.2	395	6H/4H	6.5	1.483	96
LPPGSQ55	32k	3.4	399	6H/5H	6.9	1.496	95
LPPGSQ64	41k	3.6	400	9H/9H	8.3	1.509	95
LPPGSQ73	23k	2.8	402	7H/6H	7.3	1.522	96
LPPGSQ82	15k	2.6	410	6H/3H	7.1	1.535	95
LPPGSQ91	13k	2.5	415	4H/2H	6.9	1.549	96

[a]Molecular weights derived from GPC, calibrated with polystyrene standards [b]PDI (Mn/Mw) values derived from GPC, [c]Temperature at with 1%wt loss observed from TGA scans [d]Measured in film mode, coated on glass.

Table 2. Mw, PDI, Thermal, and Mechanical Properties of LPPCESQ Hybrids

Sample Code	Mw[a] (g/mol)	PDI[b]	T_d(°C)[c]	Pencil Hardness on glass/PET	Surface Modulus (GPa)[e]	Refractive Index	% Transmittance @ 450nm[d]
LPPCESQ19	7k	2.8	394	4H/2H	7.4	1.450	95
LPPCESQ28	10k	2.4	398	5H/4H	7.5	1.462	96
LPPCESQ37	13k	2.6	403	5H/5H	7.7	1.475	95
LPPCESQ46	19k	3.1	410	7H/6H	7.7	1.488	96
LPPCESQ55	24k	3.2	411	9H/7H	7.9	1.500	95
LPPCESQ64	28k	3.4	415	9H/9H	8.9	1.514	96
LPPCESQ73	21k	2.7	419	8H/6H	8.1	1.528	95
LPPCESQ82	18k	2.4	424	6H/5H	7.7	1.541	95
LPPCESQ91	14k	2.7	431	3H/3H	7.4	1.554	96

[a]Molecular weights derived from GPC, calibrated with polystyrene standards [b]PDI (Mn/Mw) values derived from GPC, [c]Temperature at with 1%wt loss observed from TGA scans [d]Measured in film mode, coated on glass.

As shown in Fig. 5, the surface properties of photocured LPPGSQ64 on PET substrates revealed that the coated surface was impeccable with no discernible pinholes or cracks. Moreover, in both the submicron and micron scales, LPPGSQ64 was found to be coated extremely cleanly without any surface roughness, most likely due to the fact that these hybrid materials were highly soluble in organic solvents, which enables optimal coating conditions.
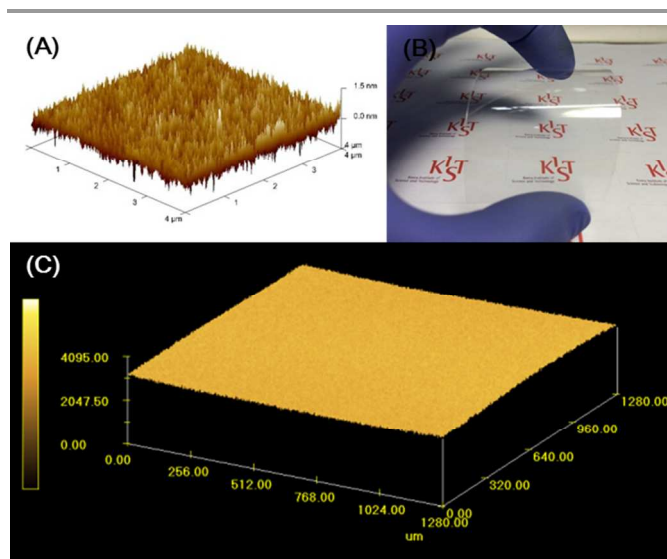

Fig. 5 Surface properties of photocured LPPGSQ64 on PET substrates (A) 3D AFM height image, (B) optical photograph, and (C) 3D confocal image.

The thermo-mechanical properties of these hybrid films are also a critical component for applications in optoelectronic applications, as thermal expansion mismatch between layers may present stress between substrates and coating layers.[5] Thus efforts to decrease the thermal expansion coefficient (CTE) of hybrid films for applications which require numerous or high temperature treatments have been ongoing. The CTE values for representative aliphatic and cycloaliphatic epoxy-functionalized polysilsesquioxanes, LPPGSQ64 and LPPCESQ64 were obtained from thermo-mechanical analysis(TMA). One of the unique features of ladder-like structured polysilsesquioxanes is that the glass transition temperature is usually derived from the flexible organic functional groups all but completely disappears after curing. This is due to the extremely rigid, highly condensed siloxane structure which restricts chain mobility. This phenomenon is unique compared with other hybrid siloxane-based sol-resins as sol-resins exhibit both α and β transitions,[17] while LPSQs do not. As shown in Fig. 6 and tabulated in Table 3, uncured LPPGSQ64 and LPPCESQ64 show both α and β transitions, with the glass transition temperatures at 108 °C and 125 °C, respectively as shown by the sharp increase slope of the TMA thermogram shown in Fig. 6. However, after photocuring, the expansion profiles for both LPPGSQ64 and LPPCE64 are linear at all temperature ranges, giving singular CTE values of 44 ppm/K and 30 ppm/K, respectively. This is an exceeding low value compared with other siloxane-based materials, as most siloxane sol-resins show a CTE value around 200 ppm/K, making these LPSQ materials very attractive for applications requiring low thermal expansion.
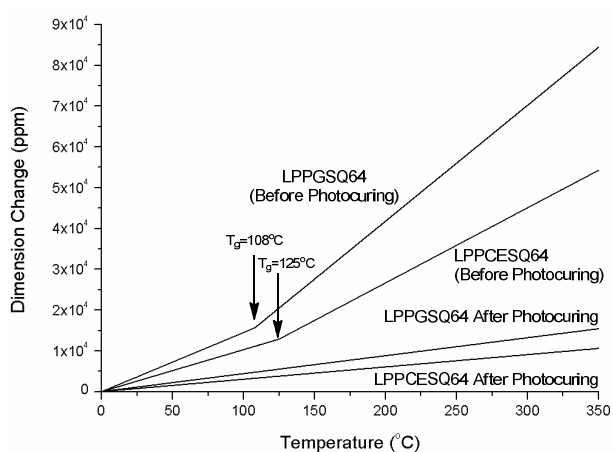
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Fig. 6 Thermo-mechanical Properties of LPPGSQ64 and LPPCESQ64 before and after photocuring

expansion under T_g before photocuring, [d]CTE^β: coefficient of thermal expansion above T_g before photocuring, [e]CTE: coefficient of thermal expansion between 0^oC and 350^oC after photocuring, [g]k: dielectric constant, measured using metal-insulator-metal method, [h]WVTR: water vapor transmission rate, [i]OTR: oxygen transmission rate

Conclusions

A series of aliphatic and cycloaliphatic epoxy-functionalized ladder-like polysilsesquioxanes, LPPGSQ and LPPCESQ copolymers were synthesized via a facile base-catalyzed sol-gel reaction. The ladder-like structure of the LPPGSQ and LPPCESQ series gave rise to the superior thermal stability (T_d > 400^oC) with thermoplastic properties and the mechanical properties in thin and bulk film state were shown to be outstanding. Thermo-mechanical analysis of these materials showed outstanding resistance to thermal expansion while the optical properties may be simply tuned by calibrating phenyl and epoxy content. Moreover, the low WVTR and OTR values obtained indicate that these materials be highly applicable as high performance barrier coats for electronic devices.

Acknowledgements

Notes and references

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1   C. Li, G.L. Wilkes, *Chem. Mater.*, 2001, **13**, 3663.
2   G. Schottner, *Chem. Mater.*, 2001, **13**, 3422.
3   J.P. Fousasser, in *Photoinitiation, Photopolymerization and Photocuring: Fundamentals and Applications*, Hanser, Much, 1995.
4   C. Decker, *Prog. Polym. Sci.*, 1996, **21**, 593.
5   W. Tanglumlert, P. Prasassarakich, P. Supaphol, S. Wongjasemji, *Surf. Coat. Technol.*, 2006, **200**, 2784.
6   A.M. Soutar, Q. Chen, R.E. Khalif, *SIMTech. Rep.* 2008, **9**, 161.
7   G. Nishino, H. Sugimoto, E. Nakanishi, *J. Appl. Pol. Sci.* 2012, **123**, 307.
8   J.S. Kim, S.C. Yang, B.S. Bae, *Chem. Mater.* 2010, **22**, 3549.
9   M. Kawamura, Y. Nakahara, M. Ohse, M. Kumei, J. Uno, H. Sakamoto, K. Kimura, I. Tanaka, *Appl. Phys. Lett.* 2012, **101**, 53311.
10   L.J. Guo, Adv. Mater. 2007, **19**, 495.
11   H.W. Ro, V. Pepova, L. Chen, A.M. Forster, Y. Ding, K.J. Alvine, D.J. Krug, R.M. Laine, C.L. Soles, *Adv. Mater.* 2011, **23**, 414.
12   G. Colucci, S. Mana, L. Conzatti, M. Sangermano, *Surf. Coat. Technol.* 2012, **206**, 2719.
13   N.B. Cramer, C.N. Bowman, *J. Polym. Sci. Part A: Polym. Chem.* 2001, **29**, 3311.
14   N.B. Cramer, S.K. Reddy, M. Cole, C.E. Hoyle, C.N. Bowman, *J. Polym. Sci. Part A: Polym. Chem.*, 2004, **42**, 5817.
15   A. Sellinger, R.M. Laine, *Chem. Mater.* 1996, **8**, 1592.
16   S.C. Yang, J.H. Jin, S.Y. Kwak, B.S. Bae, *J. Appl. Polym. Sci.*, 2012,

Besides the outstanding thermal, optical, mechanical, and thermo-mechanical properties of the synthesized LPPGSQ and LPPCESQ series, these materials exhibit highly favorable barrier properties. Typical WVTR values for siloxane resin materials have ranged around 10^1 g m^{-2} day^{-1}, necessitating the use of other inorganic fillers.[23] As shown in Table 3, obtained LPPGSQ64 and LPPCESQ64 gave WVTR values of 1.1×10^1, 1.5×10^0 g m^{-2} day^{-1}, respectively. While the WVTR value for LPPGSQ64 is conventional, the value for LPPCESQ64 is a full order below that of previous reports. Moreover, the OTR values for LPPGSQ64 and LPPCESQ64, 2.5×10^3 and 5.4×10^2 g m^{-2} day^{-1} respectively, is also very favorable compared with previous reports. The difference between the barrier properties of LPPGSQ and LPPCESQ can be attributed to the inherent structures of the epoxy groups. LPPGSQ contains glycidoxypropyl groups having a linear aliphatic carbon structure, which is a longer functionality than the cyclohexylepoxyethyl group. The shorter chain length is most likely the cause for more densely packed siloxane structures after photocuring. Moreover, the lack of uncondensed silanol groups may also be the cause for the good barrier properties, as silanol groups have high affinity for polar gases such as water vapor and oxygen.

Table 3. Properties of selected hybrid films

Property	Unit	LPPGSQ64	LPPCESQ64
$T_g{}^a$	^oC	108	125
$T_g{}^b$	^oC	-	-
$CTE^{\alpha c}$	ppm/K	145	103
$CTE^{\beta d}$	ppm/K	284	184
CTE^e	ppm/K	44	30
$R_a{}^f$ (on glass/PET)	nm	0.3/0.5	0.4/0.6
k^g	-	3.35	3.30
WVTR^h	g m^{-3} day^{-1}	1.1×10^1	1.5×10^0
OTR^i	cm^3 m^{-2} day^{-1}	2.5×10^3	5.4×10^2

[a]T_g: glass transition temperature, derived from DSC scans 10^oC/min in N$_2$, 2nd run before photocuring, [b]T_g after photocuring, [c]CTE^α: coefficient of thermal

126, 380.

17 S.C. Yang, J.H. Jin, S.Y. Kwak, B.S. Bae, *Macromolecul. Res*., 2011, **19**, 1166.

18 T. Kelen, in *Polymer Degradation*, Van Nostand Resinhold Co., New York, **1983**, 107.

19 R.H. Baney, M. Itoh, A. Sakakibara, and T. Suzuki, *Chem. Rev*., 1995, **95**, 1409.

20 Z.X. Zhang, J. Hao, P. Xie, X. Zhang, C.C. Han, and R. Zhang, *Chem Mater.,* 2008, **20**, 1322.

21 A.S. Lee, S.-S. Choi, H.S. Lee, H.Y. Jeon, K.-Y. Baek, and S.S. Hwang, *J. Polym. Sci. A. Polym. Chem*., 2012, **50**, 2653.

22 S.-S. Choi, A.S. Lee, H.S. Lee, H.Y. Jeon, K.-Y. Baek, D.H. Choi, and S.S. Hwang, *J. Polym. Sci. A. Polym. Chem.,* 2011, **49**, 5012.

23 H. Seki, T. Kajiwara, Y. Abe, T. Gunji, *J. Organomet. Chem.*, 2010, **695**, 1363.

24 K.H. Jung, J.Y. Bae, S.J. Park, S. Yoo, B.S. Bae, *J. Mater. Chem*., 2010, **21**, 1977.