

Mechanical Properties of Thiol-ene UV-Curable Thermoplastic Polysilsesquioxanes

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Key words: UV-curable, thiol-ene, polysilsesquioxanes, hybrid materials

INTRODUCTION

Scratch resistant hard-coating materials have been researched for a wide variety of applications including protective films for displays, cell phones, DVDs, and optical lenses.[1-3] These applications require not only excellent mechanical, thermal, and optical properties, but also demand easy processing and good adhesion to glass and organic polymer substrates.[4] To date, many organic plastic materials such as poly(methyl methacrylate) (PMMA) and polycarbonate (PC) materials have been investigated due to their optical transparency and easy processing.[5,6] However, many of these organic plastics exhibit poor scratch resistant properties, weak thermal stability, and low refractive indices, making application difficult. In order to attain all of these properties required of hard-coating films, the use of several additives[7] and inorganic precursors[7,8] have been extensively investigated. However, the use of additives in multi-component hard-coating solutions has led to issues such as the confirmation of miscibility and complete dispersion of the secondary components. As such, a singular component hard-coating solution is to be greatly desired.

Silsesquioxanes, with chemical formula, $[\text{SiO}_{1.5}\text{R}]_n$, represent a class of inorganic-organic hybrid materials which exhibit high optical clarity, thermal stability, and excellent mechanical properties.[9] There are three structural classes of silsesquioxanes, of which include: sol-gel processed random branched structures, cage-type polyhedral oligomeric silsesquioxanes (POSS),[10] and fully condensed ladder-like structured polysilsesquioxanes with double stranded backbones.[11-13] To date, only sol-gel derived random structures have been investigated as hardcoating formulations. However, ladder-like structured polysilsesquioxanes (LPSQs), which are of polymeric structure¹¹ consisting of an inorganic

double-stranded backbone with organic side groups, that can tune the optical, thermal, and mechanical properties of the final film, offer advantageous properties over their counterparts. In comparison with cage silsesquioxanes such as POSS structures, LPSQs exhibit superior thermal properties and processability in the form of high solubility in a wide variety of organic solvents.[12,13] And as such, LPSQ materials form excellent films with uniformity. Moreover, due to its polymeric structure, LPSQs possess a miniscule amount of end-terminated silanol groups, which do not have to be thermally cured before the film is in its final form, thus having thermoplastic properties. This is important for hardcoating applications on organic substrates such as PET, as the temperatures required for thermal curing processes ($>100^{\circ}\text{C}$) exceed the thermal stability of the substrate, while contributing to high film shrinkage.

However, despite the many advantages of ladder-structured polysilsesquioxanes, studies of their properties have been few, due to synthetic difficulties. Ever since Brown's proposal and characterization of ladder silsesquioxanes,[14] several groups have synthesized ladder-structured silsesquioxanes[11,15-18] through various routes. Recently, our group has focused on the optimization of a simple, room temperature, one-batch synthesis of high molecular weight ladder-like silsesquioxanes.[12,13] While our method allows for the facile introduction of a wide variety of organic functional groups, the structure is probably not of a perfect ladder-structure, but a ladder-like structure mixed with some amorphous polysilsesquioxanes.

Thiol-ene chemistry has been one of the hot topics in polymer chemistry today.[19-21] With a thiol group and terminal unsaturated hydrocarbon –ene group, the formation of thioether linkages to form new organic functionalities via thiol-ene click reactions have been reported as facile chemical functionalization method. Moreover, multifunctional thiols composited with multifunctional –enes are easily crosslinked under UV irradiation.[22-24] Several studies have detailed the utility and ease in which highly crosslinked films with unique microstructures may be fabricated through thiol-ene UV-curing techniques.[25] Due to the ease and mild UV conditions required for crosslinking, thiol-ene UV-curing has been examined as next generation nano-imprint lithography resins.[26] While various organic resins and formulations thereof have been reported, fully hybrid type thiol-ene materials and their mechanical properties have yet to be explored in detail.

In this study, LPSQs with copolymer compositions of phenyl and methacryloxypropyl groups (LPMASQ) and their blends with new LPSQs with phenyl and mercaptopropyl groups (LPMP SQ) of various mol ratios were synthesized and evaluated as thiol-ene UV-curable hard-coating materials. In addition, we studied the optical and mechanical properties of the LPMASQ series and their blends with the LPMP SQ series as thiol-ene photocurable hard-

coating materials in order to further enhance the mechanical properties without the need for photoinitiators.

EXPERIMENTAL

Materials

Phenyltrimethoxysilane (Shin Etsu), 3-methacryloxypropyltrimethoxysilane (Shin Etsu, 98%), 3-mercaptopropyltrimethoxysilane (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 Irgacure 184 (BASF) was used as received. All other solvents (J.T. Baker) were used as received. PET substrates were graciously donated by Woongjin Chemicals.

Typical synthesis of ladder-like structured poly(phenyl-co-mercaptopropyl)silsesquioxanes (LPMPSQ)

Synthesis of LPMPSQ64, with phenyl:mercaptopropyl ratio 6:4, was conducted following a modified literature procedure.[12] Typically, in a 100ml round bottom flask, a transparent mixture of potassium carbonate (0.04g, 0.29mmol), deionized water (4.8g, 0.267 mol), and THF (16g) was prepared. To this solution, a monomer mixture of phenyltrimethoxysilane (9.52g, 0.48mol) and 3-mercaptopropyltrimethoxysilane (7.95g, 0.32mol) was added dropwise. The reaction mixture was stirred vigorously for a maximum of 48 h, 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 several times. After collection of the organic portions, drying with anhydrous magnesium sulfate, filtering, and evaporation of dichloromethane, LPMPSQ64 was obtained as a white powder (13.3g, 95% yield). ¹H NMR (CDCl₃, ppm): 0.6-1.1 (t, Si(CH₂CH₂CH₂SH, 2H), 1.4-1.6 (d, Si(CH₂CH₂CH₂SH, 1H), 1.7-2.2 (t, Si(CH₂CH₂CH₂SH, 2H), 2.3-2.8 (t, Si(CH₂CH₂CH₂SH, 2H), 7.2-8.0 (m, Si(C₆H₅), 5H), ²⁹Si NMR (ppm): -64~-70 ppm, , -77~-82 ppm.

Characterization

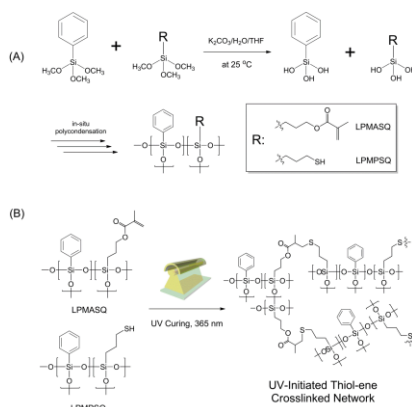
Number average molecular weight (M_n) and molecular weight distributions (M_w/M_n) of the polymers were measured by JASCO PU-2080 plus SEC system equipped with refractive index detector (RI-2031 plus), UV detector (λ =254 nm, UV-2075 plus), and Viscotek SLS apparatus using THF as the mobile phase at 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). ¹H-NMR, ²⁹Si NMR spectra were recorded in CDCl₃ at 25 °C on a Varian Unity INOVA (¹H: 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 . 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 7.5N at an angle of 45° . Nanoindentation measurements were conducted on a Hysitron Inc. TriboIndenter equipped with a Berkovich diamond tip. Measurements of elastic modulus were performed as a continuous stiffness measurement on LPSQ samples coated on silicon wafers at thickness of 100 nm. Dielectric constants were measured using metal-insulator-metal (MIM) method with thermally evaporated aluminum as metal.

RESULTS AND DISCUSSION

Synthesis and characterization of poly(mercaptopropyl)silsesquioxane (LPMP SQ)

The synthesis of highly condensed ladder-like structured poly(mercaptopropyl)silsesquioxanes has been known to be difficult under basic conditions, due to formation of insoluble gels.[27] However, the base-catalyzed system utilized in this study[12] was found to be an effective method for synthesizing ladder-structured polysilsesquioxanes with high mercaptopropyl content (Scheme 1). LPMP SQ products with high mercaptopropyl molar content (LPMP SQ19 through LPMP SQ55) were obtained as viscous liquids, while those products with high phenyl content (LPMP SQ55 through LPMP SQ91) were obtained as white powders. In addition to the LPMP SQ series, LPMASQ with various copolymer compositions of phenyl and methacryloxypropyl groups were synthesized by this same method, with full characterizations reported previously.[12] Moreover, high yields of ladder-like structured polymers make this synthetic method applicable for mass-production.



Scheme 1. (A) Synthesis of LPMASQ and LPMP SQ (B) Thiol-ene UV-curing process

With all ladder-like structured polysilsesquioxanes, all of the methoxy groups were hydrolyzed and condensed, as shown by the lack of methoxy and silanol protons at 3.55 ppm and 5.0 ppm, respectively, in the representative ^1H NMR spectra of LPMPSQ28, LPMPSQ46, LPMPSQ64, and LPMPSQ82 (Figure 1). The broad peaks centered at 7.6 ppm were assigned to the phenyl protons and the mercaptopropyl propylene protons located at 1.0 ppm, 1.92 ppm, and 2.75 ppm. Also, the thiol proton at 1.6 ppm was found to remain intact under the basic conditions of polymerization, confirmed by the integrated ratio between methylene and thiol moieties. Moreover, the initial mol feed ratio between phenyl and mercaptopropyl moieties was also confirmed by ^1H NMR. The full hydrolysis and polycondensation of the LPMPSQ series is an important prerequisite for highly uniform film formation, as unhydrolyzed –methoxy or uncondensed silanols contribute greatly to film shrinkage and cracks even before UV-curing. Through this versatile method, we were able to obtain LPMPSQ of phenyl:mercaptopropyl ratio ranging from 1:9 to 9:1.

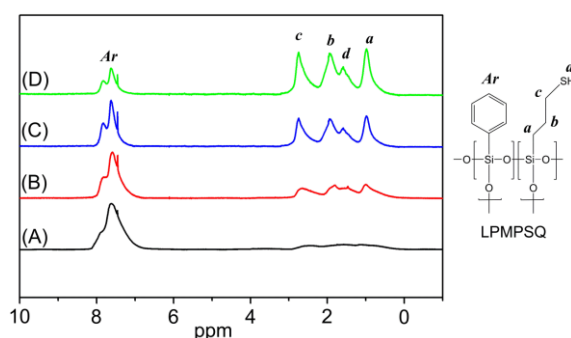


Figure 1. ^1H NMR spectra of (A) LPMPSQ28, (B) LPMPSQ46, (C) LPMPSQ64, and (D) LPMPSQ 82

FT-IR has also been known to be a good tool for analysis of ladder-like structured polysilsesquioxanes. The FT-IR spectrum of various LPMPSQs (Figure 2) shows the two sharp siloxane peaks at 1150 cm^{-1} and 1040 cm^{-1} assigned to the horizontal and vertical stretching modes of the siloxane bond, representative of ladder-like structured polysilsesquioxanes[15,19]. Also, the lack of peaks at 3500 cm^{-1} and 940 cm^{-1} is suggestive of negligible to no silanol groups, indicative of ladder-like structures[15]. Also, as expected, the intensity of the characteristic peaks at 1451 cm^{-1} and 1500 cm^{-1} from the aromatic C=C stretching mode of the phenyl groups and the 2550 cm^{-1} peak arising from the thiol moiety were shown.

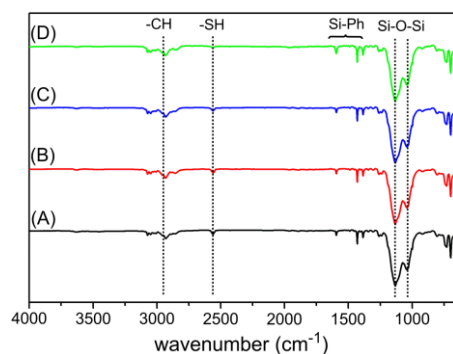


Figure 2. FT-IR spectra of (A) LPMPSQ28, (B) LPMPSQ46, (C) LPMPSQ64, and (D) LPMPSQ 82

The siloxane structure and degree of condensation were analyzed by ^{29}Si NMR. For polysilsesquioxanes, the characteristics peaks of T^3 ($\text{Ph-Si}(\text{OSi-})_3$) and T^2 ($\text{Ph-Si}(\text{OSi-})_2\text{OH}$) structures are centered at -77 and -70 ppm respectively, and the T^3 (alkyl-Si(OSi-) $_3$) and T^2 (alkyl-Si(OSi-) $_2\text{OH}$) for the mercaptopropyl-Si structures are centered at -68 and -58 ppm respectively.[12] As shown in Figure 3, only the T^3 peaks of ($\text{Ph-Si}(\text{OSi-})_3$) and (alkyl-Si(OSi-) $_3$) are shown, indicating that the siloxane structures were fully condensed. Moreover, the integrated ratio between T^3 of ($\text{Ph-Si}(\text{OSi-})_3$) and T^3 (alkyl-Si(OSi-) $_3$) reflected the initial copolymerization molar feed ratio. However, as several previous reports[18] of perfect ladder structured polysilsesquioxanes have claimed that the sharpness of the half maximum full width ($\Delta_{1/2}$) of the ^{29}Si NMR peaks determine the regularity of ladder structure, the LPMPSQ series synthesized in this study can be said to be containing some irregular amorphous structured materials mixed, because the $\Delta_{1/2}$ for the T^3 (alkyl-Si(OSi-) $_3$) and T^2 (alkyl-Si(OSi-) $_2\text{OH}$) for LPMPSQs obtained in this study were 290 Hz and 360 Hz, which were slighter higher than those compared with perfect ladder structures.[11,16-18]

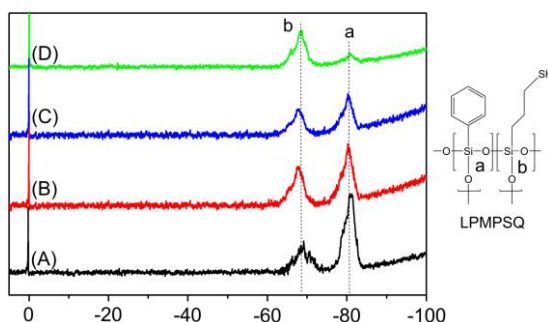


Figure 3. ^{29}Si NMR spectra of (A) LPMPSQ82, (B) LPMPSQ64, (C) LPMPSQ46, and (D) LPMPSQ28

Optical properties of LPMASQ/LPMPSQ blend films

In order to obtain the optimal mechanical and optical properties of the LPMASQ/LPMPSQ blends, the refractive indices of both LPMASQ and LPMPSQ series were measured (Figure 4).

As expected, the refractive indices of the LPMASQ and LPMPQS series increased linearly with increasing phenyl content. This refractive index match between LPMASQ and LPMPQS samples with equal phenyl molar content indicated that those samples with the similar refractive indices such LPMASQ37 and LPMPQS37 would give the best optical clarity both before and after photocuring. Interestingly enough, while blends between LPMASQ and LPMPQS samples with different refractive indices, such as LPMASQ46 and LPMPQS82 were transparent before photocuring, the transparency was not maintained after photocuring. Also, the blend compositions were based on the 1:1 molar ratio between the calculated methacryl and thiol content of the LPMASQ and LPMPQS, respectively in order for all of the methacryl and thiol groups to be photocured. In addition to the refractive indices, we measured the dielectric properties of LPMASQ/LPMPQS blend samples after UV-curing. As shown, all of the dielectric constants were between 2.5 and 3.6, and dielectric constant increased with increasing phenyl constant, as expected.

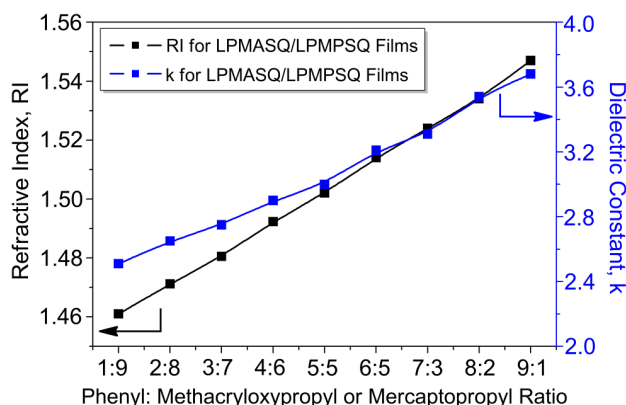


Figure 4. Refractive Indices and Dielectric Constant values for LPMASQ/LPMPQS Blends

Thiol-ene UV-Curing of LPMASQ and LPMASQ/LPMPQS Blends

Photocuring experiments were conducted using LPMASQ and LPMASQ/LPMPQS blend films with 40um thickness on both glass and PET films. Photocuring was monitored by FT-IR by both the disappearance of the C=C peaks for the LPMASQ series and the -SH peaks. Figure 5 shows the representative FT-IR spectrum for before and after the photocuring experiments of both the LPMASQ and LPMASQ/LPMPQS blend films. As shown, the C=C vinyl peaks at $1,636\text{ cm}^{-1}$ and -SH peaks at $2,550\text{ cm}^{-1}$ disappeared completely after photocuring. While conventional methacryl, vinyl-based, or even epoxy-based UV-curing requires photoinitiators, thiol-ene chemistry is well known to initiate extremely fast²⁸ and photoinitiators were not required for the LPMASQ/LPMPQS blend samples to completely crosslinking under similar UV irradiation doses. This can be another advantage of the

LPMASQ/LPMPSQ blend system, as photoinitiators may act as impurities in the final film even after curing.

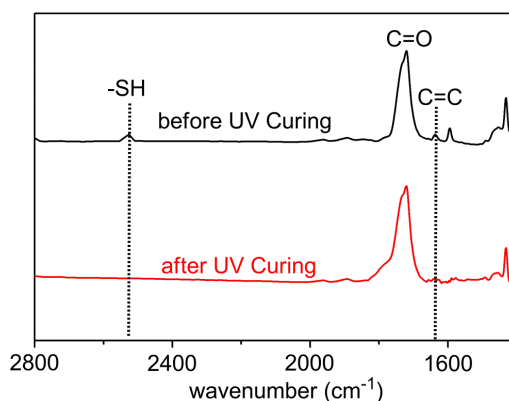


Figure 5. FT-IR spectra for LPMASQ64/LPMPSQ64 blend films (a) before photocuring and (b) after photocuring

Mechanical Properties of UV-Cured Hybrids

The pencil hardness values for these films are shown in Figure 6. Photocured LPMASQ films showed excellent hardness values ranging from 3H to 9H, even on PET substrates. This 9H value was surprising considering that pencil hardness values are known to be indelibly diminished by weaker substrates such as PET.[4,29] In general, the hardness of those samples coated on glass were about 1H to 2H greater than those coated on PET, a substrate effect commonly encountered for hardcoating materials. Moreover, the photocured LPMASQ films on PET substrates showed negligible curl effects, which usually occur from significant amounts of film shrinkage during both thermal and photo-crosslinking processes. This lack of curl can be attributed to the unique ladder structure of the polymers used, as LPMASQ and LPMPSQ are of high molecular weight with unperceivable amounts of uncondensed silanol groups, which are often the cause of substantial film shrinkage.

The blends of LPMPSQ to the corresponding LPMASQ showed even more interesting properties compared to that of neat LPMASQ films. The addition of LPMPSQ substantially increased the pencil hardness values of neat LPMASQ by about at least 1H. This increase in hardness was more clearly seen for those compositions with low phenyl content, such as the 19, 28, 37 series, as these samples showed an increase in hardness of 2H. Moreover, the substrate effect of PET coated films having lower hardness was diminished for the LPMASQ/LPMPSQ blend films. While the hardness of most of LPMASQ series gave either a 1H or 2H lower hardness value for those coated on PET, almost all of the blend films, with the exception of 55 and 91, which exhibited the same hardness. This increase in hardness and the

mitigation of substrate effect can be attributed to the fact that thiol-ene polymerizations are governed by a free radical step growth mechanism, which assures a very rapid formation of a uniform crosslinked network with low shrinkage.[30,31]

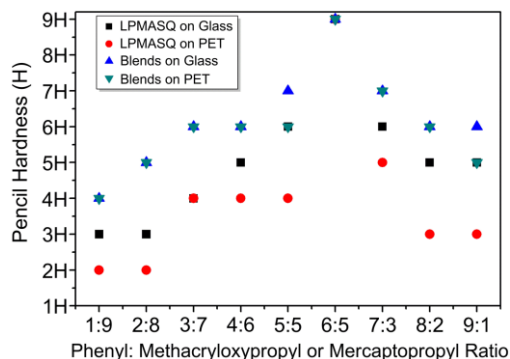


Figure. 6. Pencil Hardness Data for LPMASQ and LPMASQ/LPMPSQ blend films on glass and PET films.

Nanoindentation experiments were carried out in order to investigate the mechanical properties of the surface in detail, as it has been a well-established method for investigating the mechanical properties of hybrid films.[32,33] As shown in Figure 7, the nanoindentation modulus and hardness values were plotted as a function of phenyl:methacryloxypropyl mol ratio for the LPMASQ only films (Figure 7A) and phenyl:methacryloxypropyl/mercaptopropyl mol ratio for the LPMPQS blend films (Figure 7B). As shown the modulus values slightly decreased as the phenyl content increased from 1:9 to 3:7 at lower phenyl contents, but then increased significantly up to 7.5 GPa for LPMASQ91 and 6 GPa for LPMASQ91/LPMPQS91 blend films. This is an interesting result as this decrease and increase in modulus as a function of phenyl content was in contrast with the pencil hardness results which generally showed an increase and then slight decrease in the pencil hardness as phenyl content increased. This can be attributed to the state of the LPMASQ as for those samples with phenyl content under 5:5 are in the liquid state, while those above are solid powders. It seems as the increase in phenyl content invariably increases the surface mechanical properties when there is a substantial amount of phenyl content (above 4:6) even after UV-curing. Moreover the liquid state of the pre-cured polymer may induce substantial shrinkage when cured, which may lead to undetectable voids thus depreciating mechanical properties, which are unnoticeable in the bulk film state for pencil hardness measurements. Also, the hardness values for LPMASQ and LPMASQ/LPMPQS blends remained relatively unchanged between 500-600 MPa, and 300-400 MPa, respectively. Another noteworthy result was that the LPMASQ samples showed slightly lower modulus and hardness values compared with the LPMASQ/LPMPQS blends. While the pencil hardness

results were relatively similar as both showed exceptional surface hardness, the nanoindentation results showed that by blending the thiol-containing LPMPQS, the modulus values decreased. This was in contrast to what was hypothesized, as the propyl-group linkage to the thiol was shorter than the only methacryl-substituted LPMASQ, but we attributed this phenomenon to the low mechanical properties of the thio-ether linkage relatively to the fully methacryl-based functionality, despite its high photocuring rates. However, when examining the brittleness index,[32] as defined as by the hardness divided by the modulus, the LPMPQS/LPMASQ blend series exhibited a substantially lower brittleness index, as shown in Table 2. This is a highly advantageous property as polysilsesquioxanes have been known to be considerably brittle, and conventional methacryl-based sol-gel materials giving a brittleness index around 0.08.[32] This lower brittleness index, and greater plasticity index may allow for more coatings on flexible substrates for next generation flexible devices.

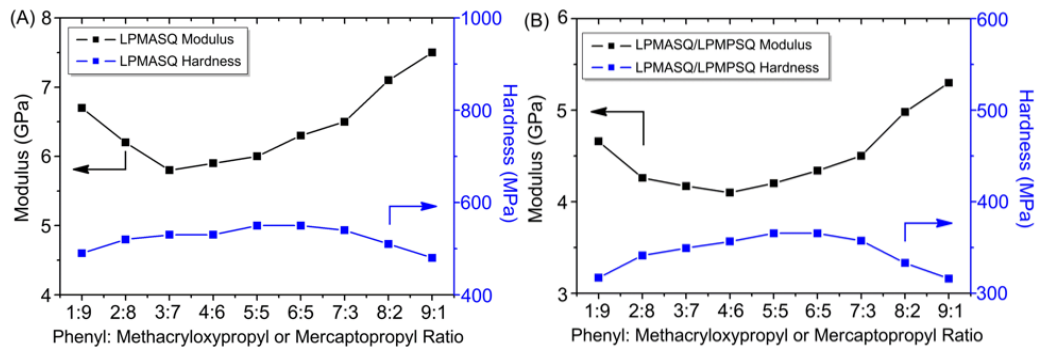


Figure 7. Nanoindentation Modulus and Hardness Values for (A) LPMASQ and (B) LPMASQ/LPMPQS Blend Films

Table 2. Brittleness and Plasticity Indices for LPMASQ and LPMASQ/LPMPQS Blends

LPMASQ	19	28	37	46	55	64	73	82	91
Brittleness Index, H/E	0.073	0.084	0.091	0.090	0.092	0.087	0.083	0.072	0.064
Plasticity Index, E/H	13.7	11.9	10.9	11.1	10.9	11.5	12.0	13.9	15.6
LPMASQ/LPMPQS Blends	19	28	37	46	55	64	73	82	91
Brittleness Index, H/E	0.056	0.065	0.068	0.070	0.070	0.068	0.065	0.056	0.050
Plasticity Index, E/H	17.9	15.4	14.8	14.3	14.2	14.6	15.4	18.0	19.9

CONCLUSION

A series of thiol-ene UV-curable thermoplastic poly(phenyl-co-methacryloxypropyl)silsesquioxanes (LPMASQ) and their blends with newly synthesized poly(phenyl-co-mercaptopropyl)silsesquioxanes (LPMP SQ) were evaluated as inorganic-organic hybrid photocurable hardcoating formulations. These materials exhibited excellent transparency, high refractive index, and superior pencil hardness in comparison with other organic and multi-formulations. Mechanical properties of these hybrid formulations revealed a dependence on the organic functional group composition in which high phenyl content and lack of thiol groups led to the highest modulus and hardness values. However, with the introduction of thiol-groups and their blends with methacryl-based LPSQs revealed a substantial decrease in brittle index. These excellent optical, mechanical properties, as well as facile synthetic procedure and high yields make these materials suitable for industrial application in next generation flexible hybrid coatings.

REFERENCES

- [1] C. Li and G.L. Wilkes, *Chem. Mater.*, **13**, 3663, 2001.
- [2] G. Schottner, *Chem. Mater.*, **13**, 3422, 2001.
- [3] N. Hayashida, H. Hirata, T. Komaki, M. Usami, T. Ushida, H. Itoh, K. Yoneyama, and H. Utsunomiya, *Jpn. J. Appl. Phys.*, **42**, 750, 2004.
- [4] S. Sepeur, N. Kunze, B. Wurner, and H. Schmidt, *Thin Solid Films*, **351**, 216, 1999.
- [5] K. Budinski, *Surf. Coat. Technol.*, **188**, 539, 2004.
- [6] G. Nushino, H. Sugimoto, and E. Nakanishi, *J. Appl. Polym. Sci.*, **123**, 307, 2012.
- [7] S.J. Jeon, J.J. Lee, W. Kim, T.S. Chang, and S.M. Koo, *Thin Solid Films*, **516**, 3904, 2008.
- [8] C.C. Chang, T.Y. Oyang, F.H. Hwang, C.C. Chen, and L.P. Cheng, *J. Non-Crys. Solids*, **358**, 72, 2012.
- [9] R. H. Baney, M. Itoh, A. Sakakibara and T. Suzuki, *Chem. Rev.*, **95**, 1409, 1995.
- [10] D.B. Cordes, P.D. Lickiss, F. Bataboul, *Chem. Rev.*, **110**, 2081, 2010.
- [11] Z. X. Zhang, J. Hao, P. Xie, X. Zhang, C. C. Han and R. Zhang, *Chem Mater.*, **20**, 1322, 2008.
- [12] S. S. Choi, A. S. Lee, H. S. Lee, H. Y. Jeon, K. Y. Baek and S. S. Hwang, *J. Polym. Sci. Part A: Polym. Chem.*, **49**, 5012, 2011.

- [13] S. S. Choi, H. S. Lee, S. S. Hwang, D. H. Choi and K. Y. Baek, *J. Mater. Chem.*, , **20**, 9852, 2010.
- [14] J.F. Brown, L.H. Vogt., A. Katchman, J.W. Eustance, K. M. Kiser, and K.W. Krantz, *J. Am. Chem. Soc.*, **82**, 6194, 1960.
- [15] V.N. Tsvetkov, K.A. Andrianov, G.I. Okhrimenko, and M.G. Vitovskaya, *Eur. Polym. J.*, **7**, 1215, 1971.
- [16] S. Chang, T. Matsumoto, H. Matsumoto and M. Unno, *Appl. Organometal. Chem.*, **24**, 241, 2010.
- [17] M. Unno, T. Matsumoto, and H. Matsumoto, *J. Organomet. Chem.*, **692**, 307, 2007.
- [18] H. Seki, T. Kajiwarra, Y. Abe, and T. Gunji, *J. Organomet. Chem.*, **695**, 1363, 2010.
- [19] C.E. Hoyle and C.N. Bowman, *Angew. Chem.*, **49**, 1540, 2010.
- [20] M.J. Kade, D.J. Burke, and C.J. Hawker, *J. Polym. Sci. Part A: Polym. Chem.*, **48**, 743, 2010.
- [21] A.B. Lowe, *Polym. Chem.*, **1**, 17, 2009.
- [22] N.B. Cramer, S.K. Reddy, A.K. O'Brien, and C.N. Bowman, *Macromolecules*, **36**, 7964, 2003.
- [23] K.M. Schreck, D. Leung, and C.N. Bowman, *Macromolecules*, **44**, 7520, 2011.
- [24] B.G. Rutherglen, R.A. MacBath, Y.L. Huang, and D.A. Shipp, *Macromolecules*, **43**, 10297, 2010.
- [25] F. Alves and I. Nischang, *Chem. Eur. J.*, **19**, 17310, 2013.
- [26] P. Wangyang, Y. Gan, Q. Wang, and X. Jiang, *J. Mater. Chem. C.*, **2**, 6140, 2014.
- [27] Moriya, M. Kuga, S.I. Yamamoto, M. Kashio, A. Kamejima, and T. Sugizaki, *Polymer*, **47**, 1837, 2006.
- [28] N.B. Cramer, S.K. Reddy, M. Cole, C.E. Hoyle, and C.N. Bowman, *J. Polym. Sci. Part A: Polym. Chem.*, **42**, 5817, 2004.
- [29] L.Y.L. Wu, G.H. Tan, X.T. Zeng, T.H. Li, and Z. Chen, *J. Sol-Gel Sci. Technol.*, **38**, 85, 2006.
- [30] G. Colucci, S. Mana, L. Conzatti, and M. Sangermano, *Surf. Coat. Technol.*, **206**, 2719, 2012.
- [31] N.B. Cramer and C.N. Bowman, *J. Polym. Sci. Part A: Polym. Chem.*, **29**, 3311, 2001.
- [32] X. Zhang, L. Hu, and D. Sun, *Acta Mater.*, **54**, 5469, 2006