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A Study on Liquid Hybrid Material for Waveguides—Synthesis and Property of PSQ-Ls for Waveguides

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Silicate-based inorganic-organic hybrid polymer systems have many unique properties including thermal stability and photo-stability, chemical resistance with the combination of tunable optical properties. Two kinds of new UV-patternable hybrid materials PSQ-Ls were synthesized by a sol-gel process at room temperature, which can be used for low cost fabrication of optical waveguides. Thick films (up to 8.31 μm) can be coated by a single spin-coating process without any cracking and the average surface roughness (Ra), detected by atomic force microscopy (AFM), is below 0.5 nm. The optical properties (refractive index, birefringence, and optical loss at 1310 nm and 1550 nm, respectively) of the PSQ-Ls films are investigated by a prism coupler. The refractive index of PSQ-Ls can be exactly tuned from 1.4483 to 1.5212 by blending PSQ-LH ($n_{TE} = 1.5212$ @ 1310 nm) and PSQ-LL ($n_{TE} = 1.4483$ @ 1310 nm). The maximum refractive index contrast is about 4.8%. After post-baking, birefringences of the films are below 0.0005 and optical losses are about 0.2 dB · cm^{-1} at 1310 nm, 0.7 dB · cm^{-1} at 1550 nm, respectively. Furthermore, the PSQ-Ls films also show outstanding thermal stability in air atmospheres.

Keywords: hybrid material; sol-gel; waveguide; hybrid polymerization

1 Introduction

Organic polymers have been explored for many years as alternative materials for fabrication of optical components. With all the promise of polymers, to date there has been limited acceptance of these materials in the established telecommunication market. The fatal fact can be attributed to their reliability because of their photo-oxidative degradation when exposed to high flux (1). However, when engineers have been cautious about utilizing polymer due to the reliability needs, siloxanes polymers which are capable of passing Telcordia specifications (2), give engineers a new promise. Thus, siloxanes polymers, which are viewed as inorganic-organic hybrid polymers (also known as polysiloxanes), have attracted great attention for their application in making optical waveguides owing to their excellent thermal stability accompanied by optical properties (3–6). By combining the characteristics of inorganic glass and organic polymer, the silicate-based inorganic-organic hybrid polymer provides many advantages over pure traditional inorganic glass or organic polymer films. For instance, the hybrid material overcomes two main problems of inorganic glass films: low mechanical flexibility and the cracking of thick layer above 2 μm, and high temperature processing requirement (generally above 600°C) (3, 7). Compared with a pure organic polymer coating, the hybrid material also manifests advantages such as low optical propagation loss, extremely excellent chemical and thermal stability, as well as good compatibility with different substrates such as silicon wafer, quartz, and print circuit board (PCB) (3, 8, 9). In addition, the optical properties of the hybrid materials (such as transmittance and refractive index) can be widely tuned through a combination of changing its organic groups and modifying their structures.

Sol-gel processing offers a low temperature route to the development of silicate-based inorganic-organic hybrid polymer potentially suitable for fabricating optical waveguides at low cost (10, 11). By bonding photosensitive organic groups in the material, usually with unsaturated C=C bonds, the hybrid materials can be polymerized upon UV light irradiation, and this characteristic is necessary for direct pattern wave-guide structures on planar substrate.

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In this study, we prepared novel liquid hybrid material polysiloxanes (named as PSQ-Ls) derived from different feed ratios of phenyl trimethoxysilane (PTMS), methyl trimethoxysilane (MTMS) and 3-(methacryloxy) propyl trimethoxysilane (MAPTMS) for waveguides by an alternative sol-gel synthetic process. Thick films (up to 8.31 μm) could be coated by a single spin-coating process without any cracking. Si-OH groups generated in the hydrolysis stage were practically completely reacted and disappeared after an elaborate heat treatment process, and the optical absorption losses of their films were efficiently controlled at a low value. Their refractive indice could be tuned through blending two PSQ-Ls with different refractive index, such as PSQ-LH ($n_{TE} = 1.5212$ @ 1310 nm) and PSQ-LL ($n_{TE} = 1.4483$ @ 1310 nm). Furthermore, their surface and thermal properties were studied by atomic force microscopy (AFM) and thermogravimetric analysis (TGA).

2 Experimental

2.1 Preparation of PSQ-Ls

PSQ-Ls were synthesized by a sol-gel process from phenyl trimethoxysilane (PhTMS), methyl trimethoxysilane (MTMS) and 3-(methacryloxy)propyl trimethoxysilane (MAPTMS) (Scheme 1). The mixture of the above-mentioned starting materials combined with 0.1 M aqueous hydrogen chloride (pH = 1.0) in a sealed container, was stirred for 2 h at 25°C. The resulting solvent was dissolved in an equal volume of ether and then washed by deionized water until pH was 6–7. The solvent was then removed under vacuum at 40°C and transparent liquid PSQ-Ls were obtained. The methoxysilanes feeds and molar ratio of water to methoxysilane (represented by R) are shown in Table 1. The thickness of PSQ-Ls can be controlled from below 1 micrometer to several micrometers by spinning rate and time.

2.2 Curing Process of PSQ-Ls Films

A 0.8 wt% photoinitiator PI-184 (1-hydroxycyclo-hexylphenylketone, IGM) was mixed with PSQ-Ls and the resulting liquid was filtered through a 0.22 μm microfilter to remove the dust. The transparent lacquer was spin-coated on a Si or quartz substrate followed by pre-bake at 80°C in a convection oven for several minutes. The layer was then exposed to UV light ($\lambda = 365$ nm, power density approximately 25 $mW \cdot cm^{-2}$) for 120 s in nitrogen. After the UV illumination, the sample was post-baked in the convection oven at 180°C for 2 h, and at 200°C for 2 h.

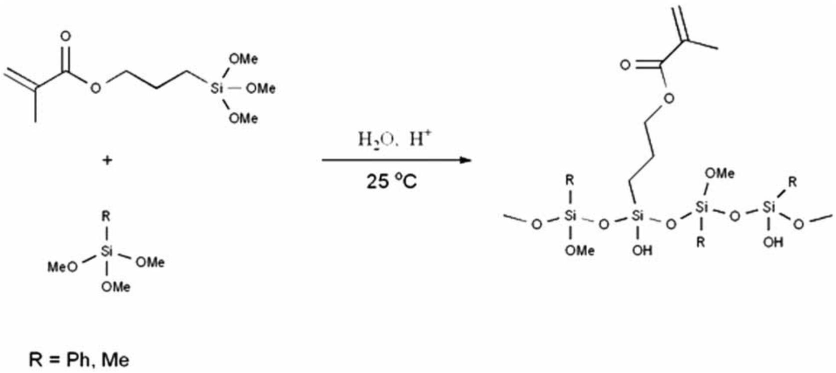
2.3 Characterization

FTIR Spectra were measured with a NICOLET-20DXB FTIR Spectrometer. ^{1}H-NMR spectra were obtained with a Varian Unity Inova 400 spectrometer at an operating temperature of 40°C, and recorded in $CDCl_3$ solutions at a resonance frequency of 399.716 MHz and a 30° pulse, and a delay of 10s were used to acquire the quantitative spectra. Atomic force microscopy (AFM, Nanoscope-IIIa, Digital Instruments) were used for the analysis of the surface morphologies of the PSQ-Ls films spin-coated on Si wafers and cured as in the above process. Thermogravimetric analysis (TGA) was performed on the Perkin-Elmer 7 Series Thermal Analysis System. Decomposition temperatures (T_d) were recorded when the weight loss of the sample reached 1% in TGA. The refractive indice of the cured films were measured using a Prism Coupler SPA 4000, which generated light from 1310 nm laser diode, and 1550 nm laser diode. Optical losses of the cured films were measured at 1310 nm and 1550 nm, respectively, on slab waveguide samples using the technique of high-index liquid immersion with SPA 4000.

3 Results and Discussion

3.1 Synthesis of PSQ-Ls

Silica precursors (MTMS, PhTMS, MAPTMS), in the presence of water at pH = 1.0, undergo hydrolysis reaction and subsequently, condensation reaction as shown in Scheme 1. Equations (1), (2), and (3) also describe the details of this chemical process (12). When the silanol group hydrolyzed in the acid medium reacts with another



Sch. 1. Synthetic route of PSQ-Ls based on a sol-gel process.

Table 1. Characteristics of liquid hybrid material PSQ-Ls

	MAPTMS/MTMS/PhTMS[a]	R	Si-OMe/3(Si-C)[b]	η^c (mPa · s@25°C)	n_{TE}@1310 nm of cured film	n_{TE}@1550 nm of cured film
PSQ-LH	15/5/80	1.2	0.27	813	1.5212	1.5198
PSQ-LL	10/75/15	1.3	0.18	658	1.4483	1.4468

[a] Molar ratio.
[b] Calculated from ^{1}H-NMR.
[c] Determined by rotational viscometer.

silanol group or the methoxy group of silica precursors, a siloxane bond is formed accompanied with methanol as by-product and solvent. For a hydrolytic sol-gel process, when the reaction temperature, time and pH value of the solution are fixed, the chemical structure and viscosity of the product are mainly determined by molar ratio of water to silica precursors. To obtain PSQ-Ls with appropriate viscosity for spin-coating and UV curing, PSQ-LH with the R of 1.2 and PSQ-LL with the R of 1.3 were prepared, respectively. When the R value was higher than 1.4, the viscosity of the resulting hybrid material would be too high to spin-coat at room temperature, while the R was lower than 1.0, the molecular weight and viscosity of the material would be too low to cure by UV light. The characterization of PSQ-Ls is shown in Table 1. PSQ-LH with higher PhTMS feed possessed higher viscosity ($\eta = 813$ mPa · s) and the resulting film possessed higher refractive ($n_{TE} = 1.5212$ @ 1310 nm) compared with PSQ-LL with lower PhTMS feed. And the content of MAPTMS in PSQ-Ls was less than 15 mol% due to so many C-H bonds in MAPTMS, however, it was enough to solidify after UV exposure.

$$\equiv\text{Si-OMe} + \text{H}_2\text{O} \longrightarrow \equiv\text{Si-OH} + \text{MeOH} \qquad (1)$$

$$\equiv\text{Si-OMe} + \text{HO-Si}\equiv \longrightarrow \equiv\text{Si-O-Si}\equiv + \text{MeOH} \qquad (2)$$

$$\equiv\text{Si-OH} + \text{HO-Si}\equiv \longrightarrow \equiv\text{Si-O-Si}\equiv + \text{H}_2\text{O} \qquad (3)$$

The ^{1}H-NMR spectra of PSQ-LL and PSQ-LH are shown in Figure 1. The spectra of PSQ-LL and PSQ-LH are almost the same in the chemical shift because the two materials are the same in the H atom kinds. However, the relative intensity and the shape of the peaks may different due to the different ratios of starting three precursors for PSQ-LL and PSQ-LH. In the spectra of PSQ-LL and PSQ-LH two broad signal groups at 7.3 and 7.7 ppm are caused by H atoms in phenyl groups, while the signal at 0.2 ppm is identified as -CH$_3$. The signals at 0.7, 1.8, 1.9, 4.1, 5.5, 6.1 ppm result from the proton in the -CH$_2$CH$_2$CH$_2$-OC(O)C(CH$_3$)=CH$_2$ groups. And the broad peak centred at 3.5 ppm is the resonance of H atoms in the -OCH$_3$ units. In fact, the active H atom in SiOH isn't found in both ^{1}H-NMR.

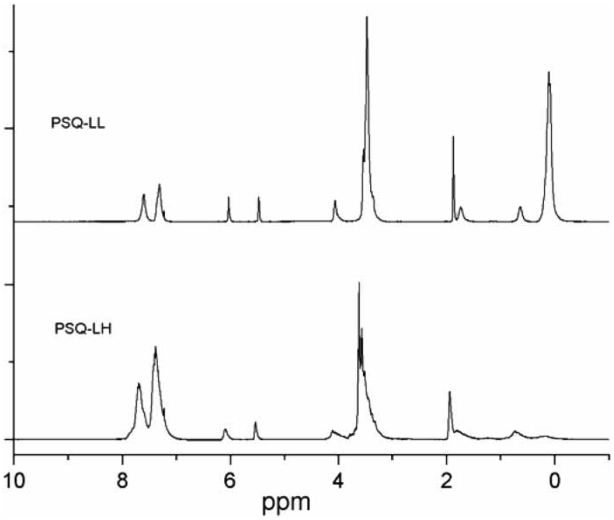


Fig. 1. The ^{1}H-NMR spectra of PSQ-LL and PS-LH.

The FTIR spectrum of PSQ-LH is shown in Figure 2(a). The band at 3436 cm^{-1} is due to the O-H stretching, and the band at 909 cm^{-1} is assigned to asymmetric Si-O stretching absorption of SiOH groups. The bands at 3051, 3073, 1593, and 1430 cm^{-1} are from phenyl groups. The absorption around 1270 and 770 cm^{-1} corresponds to the existence of SiCH$_3$ bonds. The band founded at around 1640 cm^{-1} is assigned to C=C (from MAPTMS) stretching, while the band at 1718 cm^{-1} is from C=O vibration. The sharp, distinctive absorption peak at 2840 cm^{-1} is attributed to the Si-OMe rocking, and another characteristic absorption band of SiOMe group appears near 1190 cm^{-1}. The two

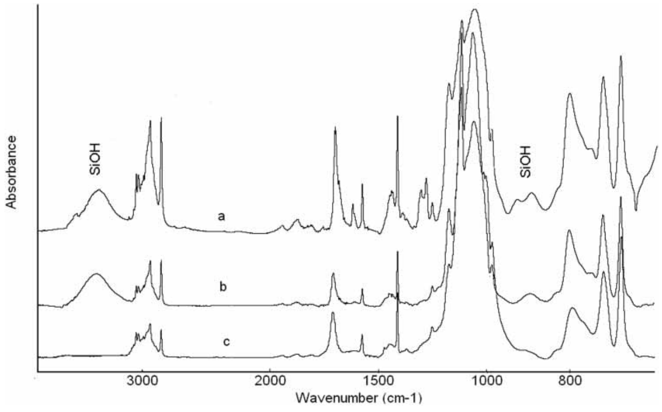
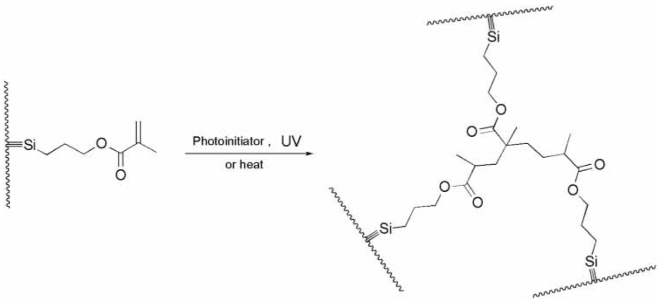


Fig. 2. FTIR spectra of PSQ-LH films after performing different steps: a) PSQ-LH; b) after UV exposure for 120 s in nitrogen; c) after post-baked at 200°C for 4 h.



Sch. 2. Curing process of methacrylic groups upon UV exposure or heat.

strong bands between 1140 and 1000 cm^{-1} arise from the asymmetric Si-O-Si stretch vibration.

3.2 *Curing Process of PSQ-Ls Films*

PSQ-Ls can be cured by a hybrid polymerization composed of free radical polymerization of C=C from MAPTMS (Scheme 2), and condensation reaction of Si-OH (Scheme 3). The FTIR absorption spectroscopes were recorded for photocuring and thermal curing processes of PSQ-LH films. The methacrylic groups in PSQ-Ls make them photopatternable. Upon UV illumination and in the presence of the photoinitiator PI-184, a free radical polymerization could easily occur and most C=C reacted after illuminated for 120 s as described in Figure 3. The peak position of C=O bond at 1718 cm^{-1} was shifted to higher wavenumber. This means that the C=O bond could not be conjugated anymore since the entire C=C double bonds were cross-linked by UV irradiation. In the heat treatment step after the UV exposure, the residue of Si-OH in the films further carried out condensation at high temperature to form glass-like material. The change of Si-OH during this stage can be observed cearly from infrared spectroscopy as shown in Figure 2. When the temperature was up to 200°C for more than 4 h, the absorption peaks at around 3436 and 909 cm^{-1} disappeared due to condensation of SiOH.

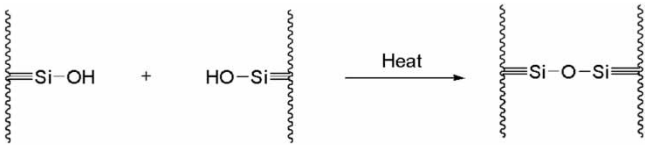
3.3 *Characterization of PSQ-Ls Films*

3.3.1 *Refractive Index Measurement of the Films*

Exactly tuning refractive indice of PSQ-Ls could be achieved by simply blending of PSQ-LH ($n_{TE} = 1.5212$ @ 1310 nm) and PSQ-LL ($n_{TE} = 1.4483$ @ 1310 nm). The similar structure between the PSQ-LH and PSQ-LL and their little residue Si-OH groups made the two liquids blend at any ratio without phase separation. The refractive index at 1310 nm decreased from 1.5212 to 1.4483 based on variation of the PSQ-LL content from 0–100 wt%. A good linear relationship, between the refractive index of the films and the weight content of PSQ-LL was observed as shown in Figure 4, and was perfectly fitted as Equation (4):

$$n_{TE}(x) = 1.5220 - 0.0727x \tag{4}$$

Where x is PSQ-LL weight content. The maximum refractive index change was about 4.8%. Moreover, all of the films exhibited reasonably small birefringences which were below 0.0005 as shown in Figure 5.



Sch. 3. Curing process of Si-OH upon heat.

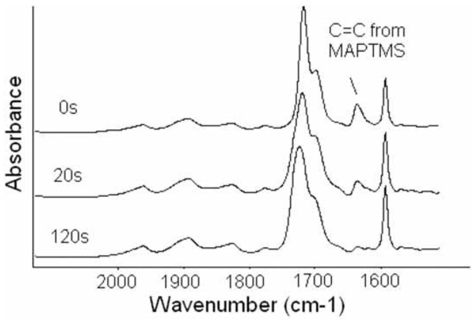


Fig. 3. FTIR spectra of PSQ-LH films after UV exposure for 0 s, 20 s and 120 s in nitrogen.

3.4 *Optical Loss of PSQ-LH Films*

Optical loss is another key property for any waveguide material. For the PSQ-Ls, absorption losses arise from vibration overtones of the aliphatic and hydroxyl groups present in the material. Absorption effects in general are more prominent at the higher wavelengths, with hydroxyl groups having an especially strong effect at the 1550 nm wavelengths (13, 14).

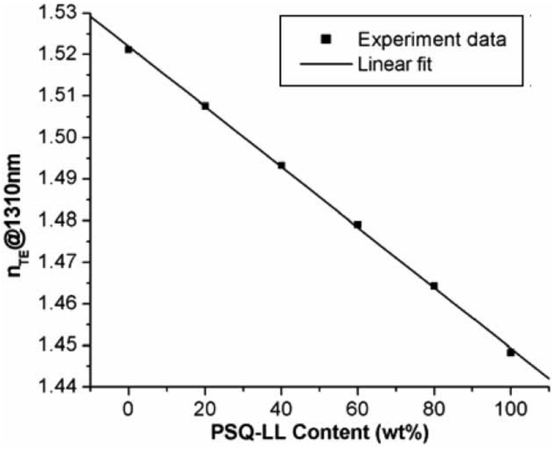


Fig. 4. The relation of refractive index and the contents of PSQ-LL (wt%).

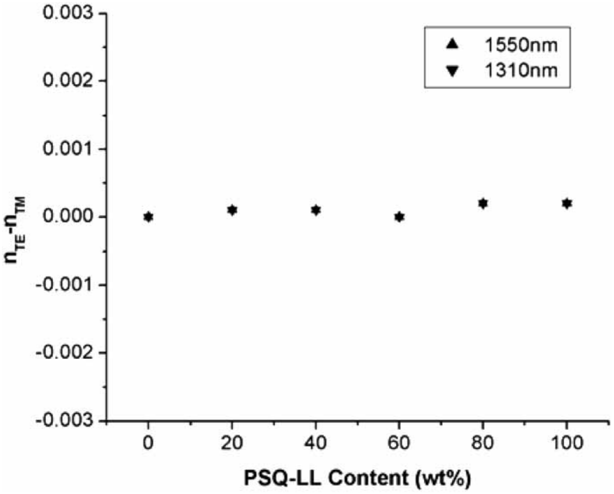


Fig. 5. Birefringence of the films with different PSQ-LL contents (wt%).

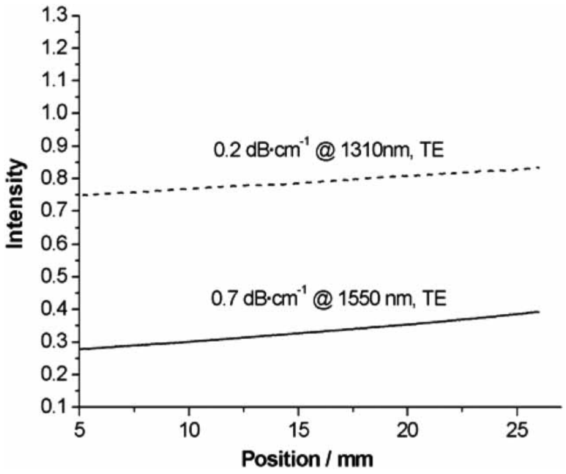


Fig. 6. Optical losses of a PSQ-LH film with post-baked at 200°C for 4 h.

The optical losses of slab waveguides (17 × 75 mm) prepared on quartz wafers were measured at 1310 nm and 1550 nm, respectively, by the high-index liquid immersion technique. We found that higher post-baking temperature and longer heating treatment time tended to decrease the optical loss both at 1550 nm and 1310 nm, especially at 1550 nm (more details about the dependence of optical loss on curing process will be discussed elsewhere). Figure 6 describes the optical losses of a PSQ-LH ($n_{TE} = 1.5206$ @ 1310 nm) film at 1310 nm and 1550 nm with a thickness of 8.31 μm, which were post-baked at 200°C for 4 h.

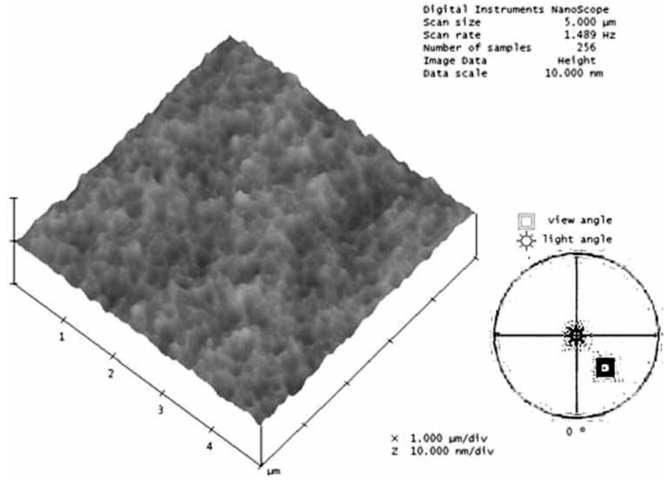


Fig. 7. AFM image of a PSQ-LL film formed on a Si wafer.

3.5 Surface Property of the Films

Figure 7 shows the AFM diagram of a PSQ-LL film spin-coated on a silicon wafer and cured as in the above process with a film thickness of 6.75 μm. The average surface roughness (Ra) and the root mean square roughness (Rq) (as shown in Table 2) of PSQ-LL were 0.406 nm and 0.521 nm, respectively. PSQ-LH film had the similar result. Obviously, the surface roughness of the PSQ-LL and PSQ-LH films obtained under the present processing condition were sufficiently small (less than 0.5 nm) for optical waveguide applications.

3.6 Thermal Property of the Films

The Thermo-Gravimetric Analysis (TGA) data of PSQ-LH and PSQ-LL films shown in Figure 8 indicates that the thermal decomposition represented by a 1% weight loss did not occur beyond 303°C for PSQ-LH film and 322°C for PSQ-LL film at a heating rate of 20°C/min in air. These results reveal excellent thermal stability of the prepared materials and meet the thermal stability requirment for waveguide fabrication.

Table 2. Properties of the prepared PSQ-LL and PSQ-LH films

	Thickness/ μm	Scan size/ μm^2	Ra/nm	Rq/nm	Z Range/nm
PSQ-LH	7.22	5.00 × 5.00	0.440	0.552	4.382
PSQ-LL	6.75	5.00 × 5.00	0.406	0.521	6.324

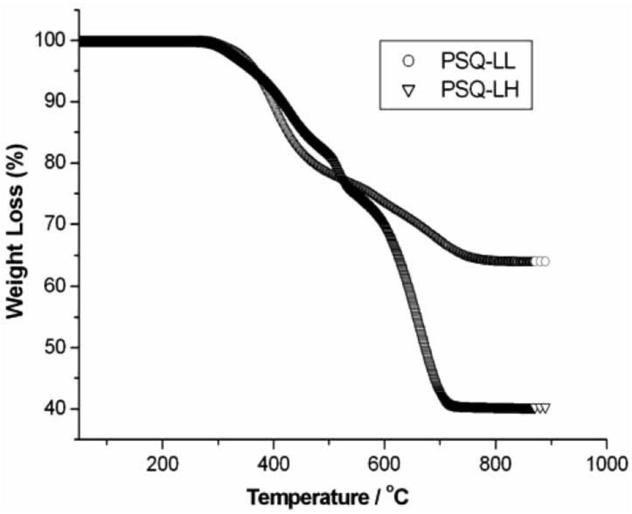


Fig. 8. TGA data of PSQ-LH and PSQ-LL cured films in air.

4 Conclusions

A new organically modified silica system (PSQ-LL and PSQ-LH) with hybrid curing characteristics (methmacrylic groups photocuring and subsequently, Si-OH thermocuring) for waveguide has been synthesized by a sol-gel process. Their refractive indice were exactly tuned from 1.4483 to 1.5212 by blending PSQ-LH ($n_{TE} = 1.5212$ @ 1310 nm) and PSQ-LL ($n_{TE} = 1.4483$ @ 1310 nm). The average surface roughness (Ra) of films obtained was below 0.5 nm from atomic force microscopy (AFM). After post-baking, birefringences of the PSQ-Ls films were below 0.0005 and optical losses of PSQ-LH ($n_{TE} = 1.5206$ @ 1310 nm) films were about $0.2\,\mathrm{dB \cdot cm^{-1}}$ at 1310 nm, $0.7\,\mathrm{dB \cdot cm^{-1}}$ at 1550 nm. The results of TGA suggested excellent thermal stability of the prepared materials. These organic–inorganic hybrid materials are promising materials for passive optical waveguide devices.

5 Acknowledgments

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6 References

1. Su, K., De Groot, J.V., Jr., Morris, A.W. and Lo, P.Y. (2006) Proc. SPIE, 6029: 60291C.
2. Goff, D.R. *Fiber Optic Reference Guide*; Focal Press: Boston, MA, 1999.
3. Zhang, X., Lu, H., Soutar, A.M. and Zeng, X. (2004) *J. Mater. Chem.*, **14**, 357–361.
4. Haas, K.-H. (2000) *Adv. Eng. Mater.*, **2**, 571–582.
5. Ou, D.L. and Seddon, A.B. (1997) *J. Sol-Gel Sci. Technol.*, **8**, 139–145.
6. Jung, J.-I., Park, O.-H. and Bae, B.-S. (2003) *J. Sol-Gel Sci. Technol.*, **26**, 897–901.
7. Yoshida, M. and Prasad, P. (1996) *Appl. Opt.*, **35**, 1500–1505.
8. Buestrich, R., Kahlenberg, F. and Popall, M. (2001) *J. Sol-Gel Sci. Technol.*, **20**, 181–186.
9. Watanabe, T., Ooba, N., Hayashida, S., Kurihar, T. and Imamura, S. (1998) *J. Lightwave Technol.*, **16**, 1049–1055.
10. Usui, M., Hikita, M., Watanabe, T., Smano, M., Sugawara, S. and Imamura, S. (1996) *J. Lightwave Technol.*, **14**, 2338–2343.
11. Kopetz, S., Rabe, E., Kang, W.J. and Neyer, A. (2004) *Electr. Lette.*, **40**, 668–669.
12. Yoshimoto, A. and Gunji, T. (2004) *Pro. Polym. Sci.*, **29**, 149–182.
13. Soppera, O. (2005) *J. Sol-Gel Sci. Technol.*, **35**, 27–39.
14. Pugliano, N., Chiarotto, N., Fisher, J. and Heiks, N. (2004) Proc. SPIE, 5358, 71–85.