Synthesis and Optical Characteristics of Trialkoxycapped Poly(methyl methacrylate)-Silica Hybrid Films

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Abstract

In this study, trialkoxycapped poly(methyl methacrylate) (PMMA)-silica hybrid films were successfully prepared for optical applications. The acrylic copolymer precursor with alkoxy side group was prepared using 2,2'-azobisisobutyronitrile (AIBN) as the initiator first. Then, it was reacted with partially hydrolyzed tetraethoxysilane solution, followed by spin coating and curing to obtain the thin films. The prepared hybrid films had high surface planarity and homogeneity. The optical properties of the prepared hybrid films could be tuned by the silica moiety. The refractive indices of the prepared films reduced from 1.495 to 1.460 by increasing the silica content. The near infrared optical spectra of the prepared films were shifted by the silica moiety. It was probably due to increase the anharmonicity of C-H bond by the silica moiety. The optical loss of the prepared optical waveguides was reduced from 0.243 to 0.198 dB/cm by increasing the silica content, which was less than that of the PMMA based waveguide. The trend on the optical loss was probably due to the reduction of the C-H number density and enhancing the anharmoncity of the C-H bond. The hybrid films prepared from the initiator of AIBN had a higher surface planarity than that from BPO and resulted in a lower optical loss of the prepared waveguides.

Key Words: Hybrid Materials, Thin Films, Optical Properties, Waveguide

1. Introduction

Organic-inorganic hybrid materials have been recognized as a new class of advanced materials [1-3]. Molecular design on the organic or inorganic moiety of the hybrid materials could produce materials with tunable properties for optoelectronic devices, including optical waveguides [4-5], high refractive index materials [6-7], electroluminescent materials[8-10], solar cells [11], and thin film transistors [12].

Our laboratory is particularly interested in synthesis of hybrid materials for optical applications [7,14-17], such as optical thin films or waveguides. Inorganic oxide, organic polymers, and hybrid materials have been recognized as three different classes of waveguide materials [18,19]. The hybrid materials could provide the following advantages over organic polymers for optical waveguide applications: (1) The incorporation of the inorganic moiety into polymer matrix could improve the thermal and mechanical properties; (2) the incorporation of inorganic moiety decreases the C-H bonding density in the waveguide materials and thus reduces the optical loss; (3) the large polarizability difference between the organic and inorganic moieties possibly induces an increase of the anharmonicity of the C-H bond and thus the NIR spectra could be shifted for the optical window of the used light source. However, it has not been proved in the literature. Note that the anharmonicity is affected by the bond type, bond angle, and polarizability.

We have successfully prepared homogeneous trialkoxysilane-capped poly(methyl methacrylate)-(PMMA)-inorganic oxide hybrid optical thin films by the combination of in-situ acid-catalyzed sol-gel process followed by spin-coating, and multi-step curing [7,13,14]. In the previous studies, the research focus was on varying the refractive index by side group or silica fraction. However, the effects of silica content on NIR optical properties and their corresponding waveguides have not been investigated yet. Besides, benzoyl peroxide (BPO) with 25% water content was used to prepare the hybrid materials [7,13,14]. The water content and high polymerization temperature of 80~90 °C by BPO might accelerate the reaction and produce large silica domain, which produced large scattering loss. Hence, a different thermal initiator is required to prepare hybrid materials for waveguide applications.

In this study, a modification of the previous reaction scheme [14] was applied to prepare the trialkoxysilane-capped PMMA-silicahybrid films, as shown in Figure 1. 3-(trimethoxysilyl) propyl methacrylate (MSMA) was polymerized with methyl methacrylate (MMA) using the 2,2'-azobis-isobutyronitrile (AIBN) initiator to form a poly (MMA-MSMA) precursor solution. Then, a partially hydrolyzed tetraethoxysilane (TEOS) was reacted with the alkoxy side chain of MSMA to produce the precursor for hybrid films. The precursor was then spun coated and cured to obtain the hybrid films. The structures and properties of the prepared hybrid materials were investigated, including FTIR, SEM, AFM, refractive index, and NIR absorption. The optical loss of the prepared

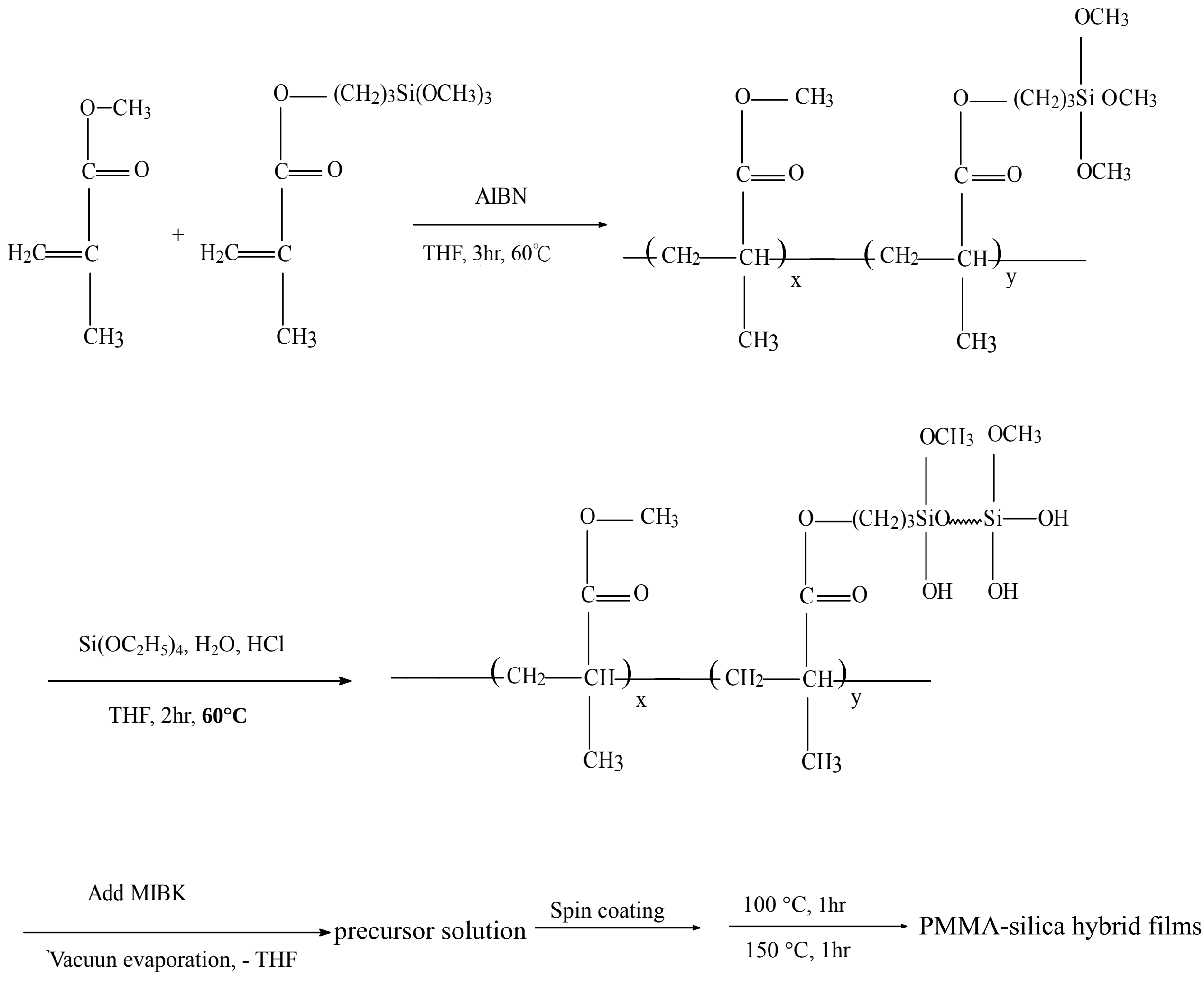

Figure 1. Reaction scheme for preparing the trialkoxycapped PMMA-silica hybrid films

optical planar waveguide was studied. The effects of the silica content on the optical properties were discussed.

2. Experimental

2.1. Materials

Methyl methacrylate (MMA, 99 wt%, Lancaster), 3-(trimethoxysilyl) propyl methacrylate (MSMA, 98 wt%, Aldrich), 2,2'-azobisiso-butyronitrile (AIBN, 99 wt%, Showa), tetrahy-drofuran (THF, 99wt%, Acros), methyl isobutyl-ketone (MIBK, 99.5 wt%, Acros), hydrogen chloride (HCl, Yakuri Pure Chemical), and tetraethoxysilane (TEOS, 98wt%, Aldrich) were used to prepare precursor solutions for the hybrid materials.

2.2 Preparation of Poly(MMA-MSMA) Precursor Solution and Their Films

The monomers, MMA, MSMA (the molar ratio of MMA to {MMA+MSMA} equal to 0.25) and AIBN (the molar ratio of AIBN to {MMA+MSMA} is 0.06) were dissolved in THF firstly. Then, the mixture was polymerized for 3 hrs at 60 °C under nitrogen atmosphere and rigorous agitation to form the poly(MMA-MSMA) precursor solution. In the following, the partially HCl hydrolyzed TEOS (the molar ratio of H_2O to {TEOS+MSMA} is 1) was added to the poly(MMA-MSMA). The overall synthesis was taken at 60 °C under nitrogen atmosphere and rigorous agitation for another 2 hrs. The denotation of **SiX** means the amount (wt%) of TEOS in the reaction mixture for preparing precursor solutions. In this study, the compositions of the prepared hybrid materials were from **Si10** to **Si30**.

In order to form high quality optical films, low boiling point THF solvent and alcohol generated from hydrolysis and condensation reaction must be removed from the precursor solution to avoid film defects by spin coating. Hence, a high boiling point solvent, MIBK, was added to the precursor solution by the weight ratio of 0.5 to THF. Then, the precursor solution was concentrated by vacuum evaporation, followed by spin coating and curing to form thin films.

2.3 Preparation of Optical Planar Waveguides

The optical planar waveguides based on the hybrid materials was prepared as below. A silicon wafer was cleaned and thermally oxidized in a circular furnace purged with water vapor and nitrogen at 1200 °C for 11 hrs to give a uniform silicon dioxide film of 1.5 μm on the wafer surface. Then, the prepared precursor solution was spun coated on top of thermal oxide at silicon wafer to form the planar waveguide. Then, it was cured at 100 °C and 150 °C for 1 hr, respectively, to form optical planar waveguides. In this case, the guiding and cladding layers were the prepared hybrid films, and thermal oxide and air, respectively.

2.4 Characterization

Infrared spectra of hybrid thin films were measured by using a Jasco Model FTIR 410 spectrophotometer. An atomic force microscope (Digital Instrument, Inc., Model DI 5000 AFM) was used to probe the surface morphology of the coated films. The microstructure of the prepared hybrid materials was further examined by a field emission scanning electron microscopy (FE-SEM, Hitachi, Model-4000). Then, it was cured at 100 ℃ and 150 ℃ for 1 hr, respectively, to form optical planar waveguides. An ellipsometer (Faertner Scientific Corporation, model number L116D) was used to measure the refractive indices of the prepared films at 632.8 nm.

For measuring the NIR absorption spectra of the prepared hybrid materials, a sample with a thickness of a few mm was obtained by evaporating the precursor solution in a 20 mL vial under vacuum. The NIR absorption spectra of the hybrid films were obtained using a UV-Visible-NIR spectrophotometer (Jasco, model No.: V-570, resolution: 0.5 nm in the NIR region) in the wavelength range of 1000 to 1800 nm. The interpretation of the NIR spectra was based on the following equation [20]:

$$\nu_v = \frac{\nu_1 v[1 - x(v+1)]}{1 - 2x} \quad (1)$$

Where ν_1, ν_v, are the fundamental and vth harmonic of the C-H stretching vibration(v = 2,3,4…). χ is the anharmonicity, which represents the deviation of the vibration from the harmonic behavior. From the FTIR and NIR spectra, theν_1 and ν_v were obtained, respectively. Then, χ was calculated from Eq. (1). The optical losses of the prepared optical planar waveguides were measured by a designed optical system (manufactured by Center of Measurement and National Standards, Industrial Technology Research Institute, Hsinchu, Taiwan) using a cutback method at 1310 nm.

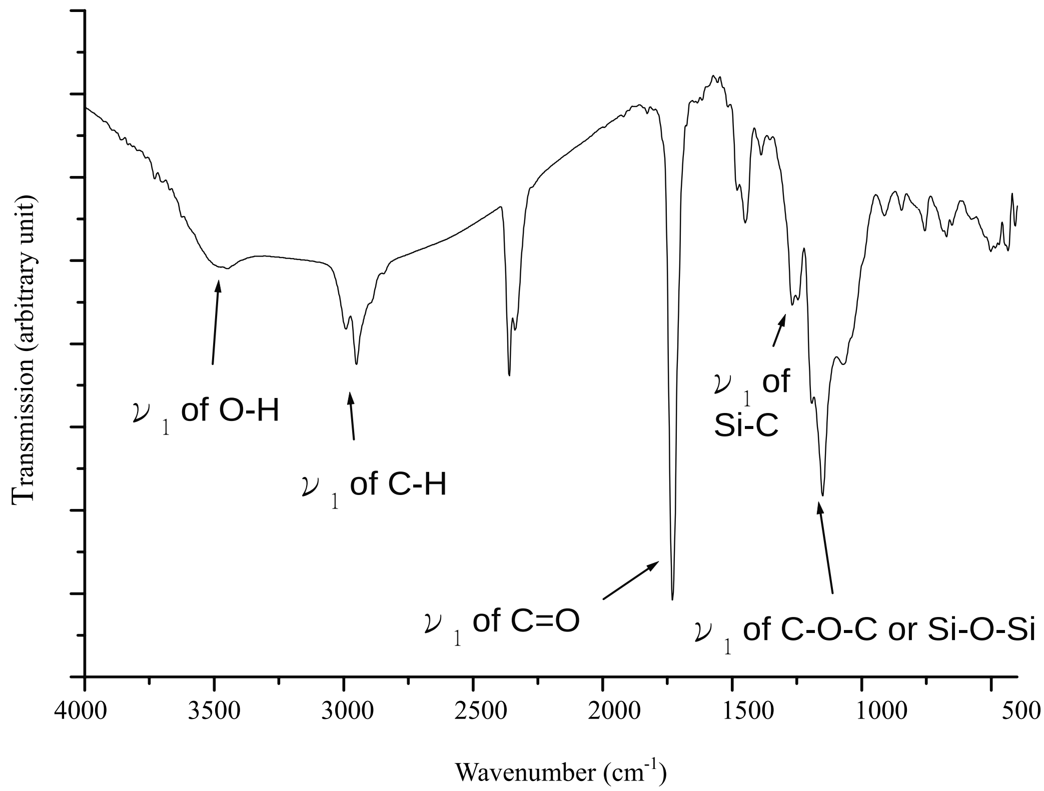

Figure 2. The FTIR transmission spectrum of the prepared hybrid film, **Si30**

3. Results and Discussion

3.1 Structural Characterization

Figure 2 shows the FTIR spectrum of the prepared hybrid materials, **Si30**. The stretching vibration bands of the C-O-C or Si-O-Si, Si-C, C=O, C-H, and O-H bonds are made around 1110, 1270, 1720, 2950, and 3500 cm^{-1} respectively. These bands are similar to those reported previously [14,17]. The Si-OH residue is due to the insufficient curing temperature of 150 °C. The position of the Si-OH band is smaller than 3520 cm^{-1}, which suggests the formation of hydrogen bonding [14]. Although the Si-OH group could not be completely polymerized, the hydrogen bonding of the Si-OH residue group with the carbonyl group makes hybrid materials with high optical transparence. The weight average and number average molecular weight of the prepared poly (MMA-MSMA) were 19272 and 10872, respectively.

The moderate molecular weight provided sufficient bonding density with silica and prevented phase separation. The film thickness of the prepared hybrid films was around 1 μm. Figure 3 shows AFM diagram of the prepared hybrid thin film, **Si15**. The surface roughness, R_a and R_q, are 0.126 and 0.169 nm, respectively. The surface roughness and properties of the prepared films are shown in Table 1.

The low roughness suggests that the high surface planarity of the prepared films. By using the BPO as the initiator, the R_a and R_q were 0.354 and 0.457 nm for the hybrid film of **Si15**. Hence, the hybrid films prepared from the initiator of AIBN has a higher surface planarity than that from BPO. The FE-SEM study showed no apparent silica domain in the prepared films. The gold particle is below 20 nm for the FE-SEM measurement. Therefore, the domain size of silica segment should be smaller than 20 nm. The AFM and SEM results suggest the homogeneous structure of the prepared hybrid materials. The DSC studies of the prepared films showed no glass transition temperature, which are similar to that reported previously [14]. The improvement of thermal properties in the hybrid materials compared to the parent PMMA is mainly resulted from the incorporation of the inorganic silica moiety.

Table 1. Properties of of the prepared hybrid materials and their corresponding waveguides

Sample	Silica (wt%)	R_a (nm)	R_q (nm)	n	Optical loss (dB/cm)
PMMA	0.00	---	---	1.495	0.652
Si10	3.35	0.126	0.162	1.494	0.243
Si15	5.22	0.098	0.122	1.493	0.240
Si20	7.24	0.176	0.223	1.480	0.205
Si25	9.43	0.074	0.094	1.464	0.213
Si30	11.81	0.126	0.169	1.460	0.198

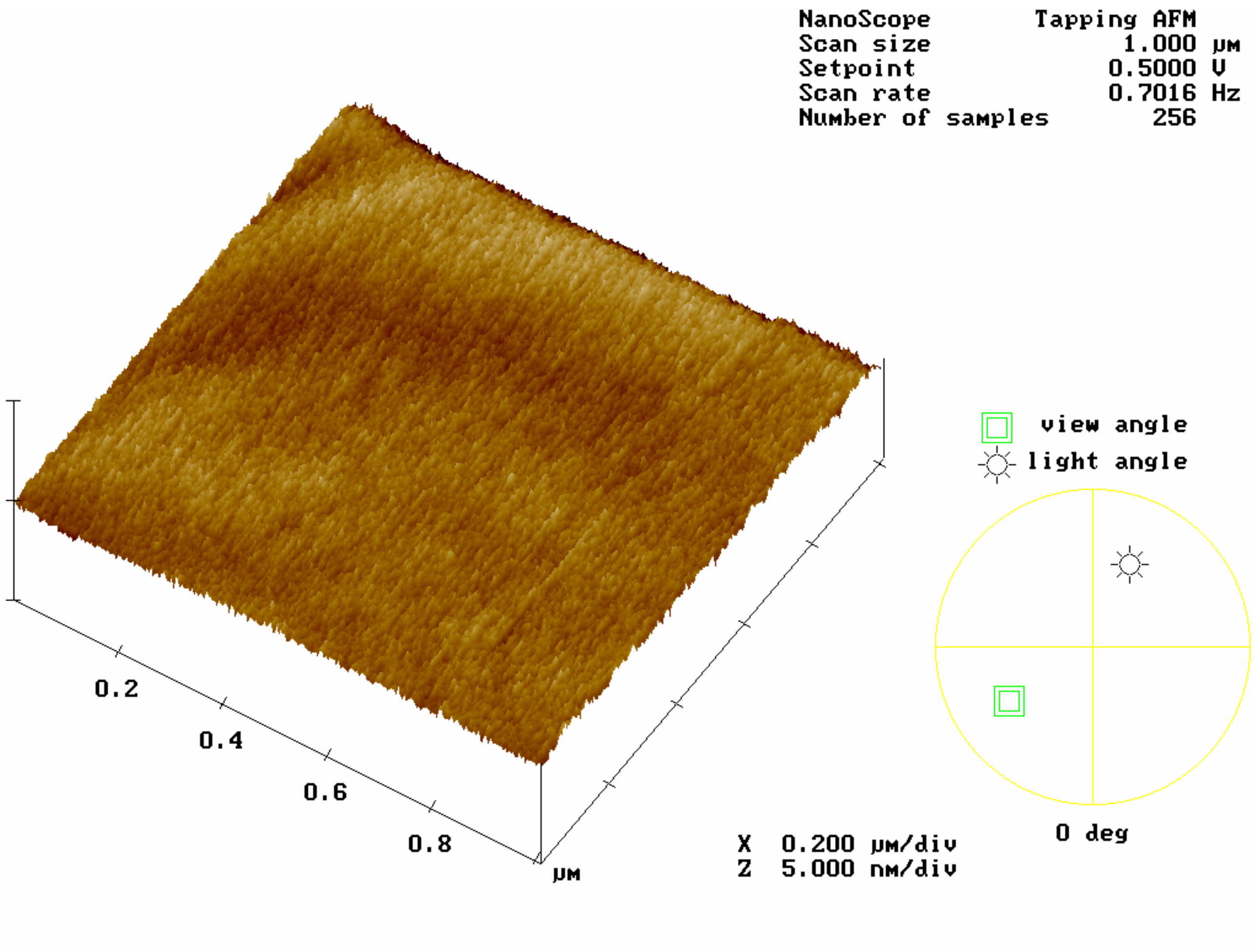

Figure 3. The AFM diagram of the prepared hybrid film, **Si15**

3.2 Optical Properties

Figure 4 shows the variation of refractive index at 632.8 nm with silica content for the prepared films. It reduces from 1.495 to 1.460 by increasing the silica content since the silica has a lower refractive index than PMMA.

Figure 5 shows the near infrared spectra of the PMMA and the prepared hybrid films. There are three absorption bands, 1100 to 1260, 1320 to1530, and 1650 to 1800 nm, as shown in the Figure. They are assigned to the second harmonic of stretching vibrational absorption (ν_3), the combination of the second harmonic of stretching vibrational absorption and bending vibrational absorption ($\nu_2+\delta$), and the third harmonic of stretching vibrational absorption (ν_2), respectively. The absorption bands of both the ν_3 and ν_2°C of C-H bands was red-shifted as the silica content increased from **Si0** to **Si30**. The fundamental C-H absorption band (ν_1) from FTIR analysis and

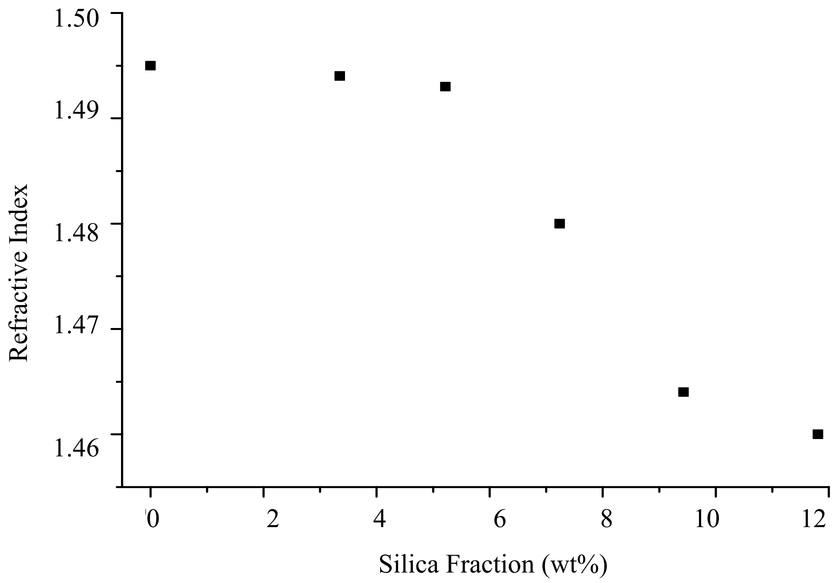

Figure 4. Variation of refractive index at 632.8 nm with silica content for the prepared films

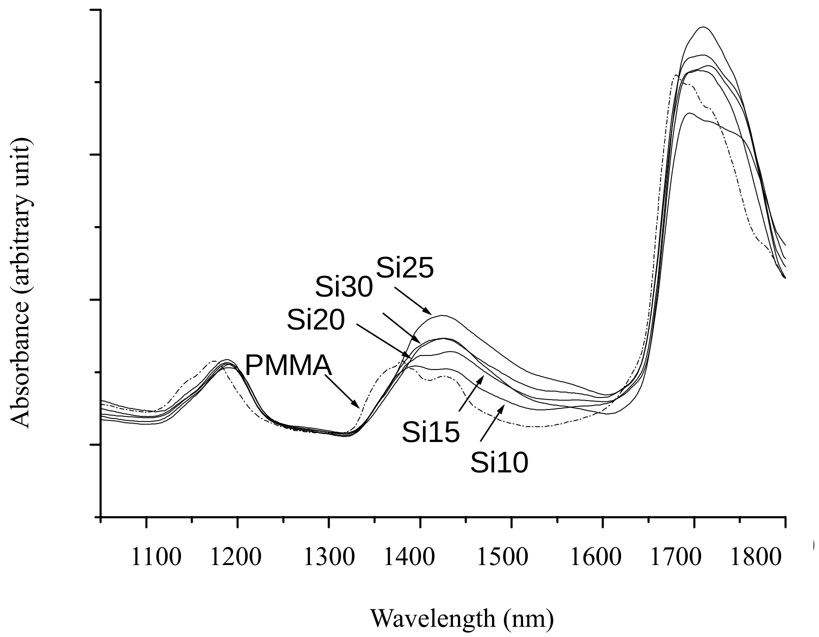

Figure 5. The near infrared spectra of the prepared films in the wavelength range of 1000~1800 nm

the third harmonic absorption band (ν_3) of C-H stretching vibration form NIR spectra were shown in Table 2. The ν_1 is almost unchanged with the silica content while the ν_3 shows a different trend of increasing. The anharmonicity, χ of the C-H bond obtained from Eq.(1) calculated increases from 0.019 to 0.026 as increasing the silica content The large difference between the polarizability of the PMMA and silica might account for the trend. The phenomena of the $\nu_2+\delta$ band shifting by the silica content results in increasing the optical transparency of hybrid materials at the optical communication wavelength of 1310 nm. The absorption band might be complicated by the ν_2 of O-H resulted from incomplete condensation of Si-OH [14,16,21], which lowered the transparency of hybrid material at 1550 nm. Although the red shifting phenomenon of the hybrid films decreases the loss at 1310 nm, they increased the optical loss at 1550 nm.

Table 2. The ν_1, ν_3 and χ from the NIR spectra of the prepared hybrid materials

Sample	$\nu_{1\ C\text{-}H}$ (nm)	$\nu_{3\ C\text{-}H}$ (nm)	χ *
PMMA	3388	1175	0.019
Si10	3389	1187	0.023
Si15	3389	1185	0.022
Si20	3389	1187	0.023
Si25	3388	1195	0.026
Si30	3388	1195	0.026

*: obtained from Eq. (1)

Nevertheless, the trialkoxycapped PMMA-Silica hybrid materials could provide a new approach for optical waveguides at communication wavelength of 1310 nm.

Figure 6 shows the variation of the transmission light intensity with the propagation length of the prepared waveguides. The linear relationship suggests the accuracy of the measurement. The obtained optical loss reduced from 0.243 to 0.198 dB/cm as increasing the silica content from 3.35 to 11.81 wt%. It suggests that the optical transparency at 1310 nm is increasing with the silica content. It is due to the red shifting of the absorption spectra as suggests from Figure 5 and thus results in reducing optical loss. Another factor for the optical loss result is the reducing the C-H number density in the polymer structure by increasing the silica content. It also indicates that increasing the silica content does not result in a decrease of optical quality and thus scattering loss is not significant in the prepared optical planar waveguides. The optical losses of the prepared waveguides based on the hybrid materials were less than that of the parent PMMA, which was 0.652 dB/cm. This suggests that the current hybrid material approach is an effective way to reduce the optical loss. By using the BPO as the polymerization initiator, the loss of the prepared waveguides was in the range of 0.371 to 0.264 dB/cm. This suggests the hybrid films prepared from BPO had a higher surface roughness than that from AIBN.

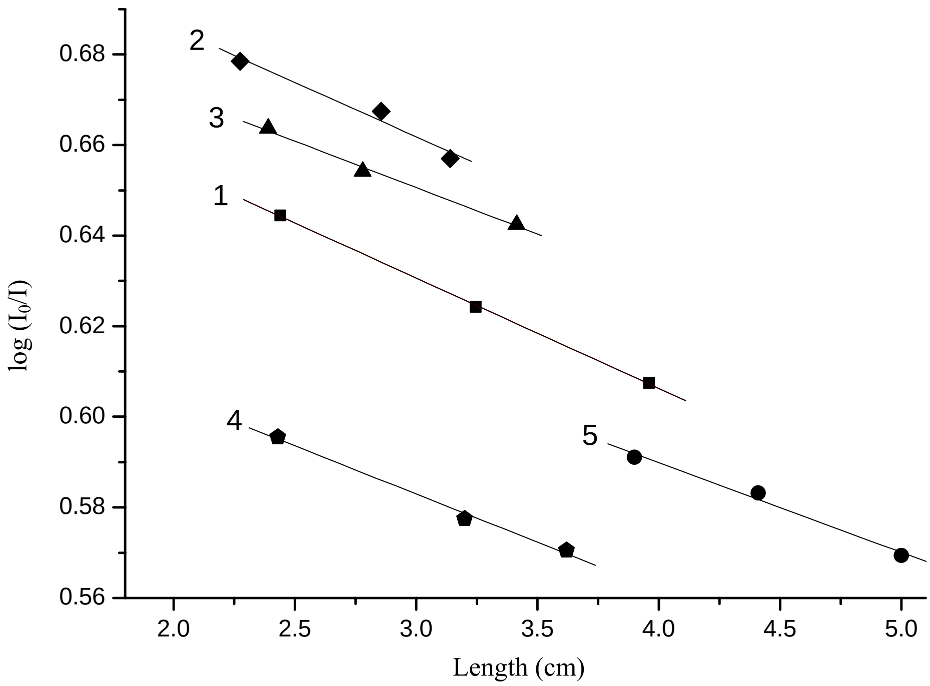

Figure 6. Variation of intensity ratio with the waveguide length for the prepared sample, **Si10**(1), **Si15**(2), **Si20**(3), **Si25**(4) and **Si30** (5)

4. Conclusions

In this study, trialkoxycapped PMMA-silica hybrid films were successfully prepared for optical applications. The prepared hybrid films had high surface planarity and homogeneity. The incorporation of the silica segment into the PMMA matrix could tune the optical properties of the prepared films, including refractive index and near infrared absorption. The refractive indices of the prepared films reduced from 1.495 to 1.460 by increasing the silica content. Shifting of the near infrared optical spectra is probably due to increase the anharmonicity of the C-H bond by the silica moiety. The optical loss of the prepared optical waveguides was reduced from 0.243 to 0.198 dB/cm as increasing the silica content. Anharmonicity and C-H number density are the major factors for controlling the optical loss. The hybrid films prepared from the initiator of AIBN had a higher surface planarity than that from BPO and thus reduced the optical loss of the prepared waveguides. The prepared films could be potentially used for optical applications.

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