Non-hydrolytic sol–gel synthesis of epoxysilane-based inorganic–organic hybrid resins

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ABSTRACT

A silica-based inorganic–organic hybrid resins (IOHR) were synthesized by non-hydrolytic sol–gel process from 3-glycidoxypropyltrimethoxysilane (GLYMO) and diphenylsilanediol (DPSD) at a fixed amount of (20 mol%) phenyltrimethoxysilane using barium hydroxide as a catalyst. The confirmation of condensation reaction in the IOHR was done by liquid state ^{29}Si NMR (Nuclear Magnetic Resonance) spectroscopy, measurement of viscosity as well as weight average molecular weight (W_m) of the IOHR. The W_m of the IOHR was varied from 1091 to 2151, depending upon the DPSD content. Fourier transform infrared (FTIR) spectroscopic measurements were performed to investigate the details of vibrational absorption bands in the IOHR. It was seen that up to 50 mol% of DPSD there were no absorption peaks in the region of 3000–3600 cm^{-1} responsible for O—H groups and it reappeared at 60 mol% of DPSD due to some unreacted OH groups present in the resin. The IOHR at all the compositions was oily transparent liquid, miscible with various organic solvents like toluene, cyclohexanone, chloroform, tehrahydrofuran (THF), etc., and also commercial epoxy resins but immiscible with water. The color of the IOHR was pale yellow, which lightened with increasing DPSD content. The IOHR having 40–50 mol% of DPSD were storable. The refractive index at 632.8 nm of the resin films varied from 1.556 to 1.588, depending upon the resin composition. Physico-chemical properties such as the thermal stability, visible transparency, etc. after curing were investigated as a function of the chemical composition.

1. Introduction

It is well known that the non-hydrolytic sol–gel process [1–3] which facilitates the synthesis of inorganic–organic hybrid resins (IOHR) without leaving any traces of solvent can produce crack-free thick-coating films with a minor shrinkage in contrast to the conventional hydrolytic sol–gel process. The IOHR materials are basically of two types [4]; (a) class I where organic modification of the siloxane inorganic matrix in the form of a dispersion of organic molecules, or interpenetrating organic polymer network, with only weak bonding to inorganic matrix and (b) class II material having organic molecules or polymer strongly bonded to the inorganic network by Si—C bonding and these silica-based hybrid materials are known as organically modified silicates, ORMOSILs. The ORMOSILs-based IOHR produces excellent and easily tunable optical properties as well as relatively high thermal stabilities in comparison to general optical polymers [5].

Many researchers synthesized IOHR and studied their properties for various applications [2,4,6]. IOHR of low hydroxyl groups using non-hydrolytic sol–gel process in 3-(trimethoxysilyl)propyl methacrylate (MPTS) and diphenylsilanediol (DPSD) in the binary system is now well established [1,2,5] where details structure and properties of the IOHR was reported. To reduce more and more hydroxyl groups, fluorinated IOHR in ternary system using MPTS and DPSD with (heptadecafluorodecyl)trimethoxysilane (HFT) adopting the same chemical route is also studied [7]. The great flexibility of the sol–gel process enables the preparation of inorganic–organic hybrids with diverse organic components. Macan et al. [8] synthesized IOHR based on an epoxy resin, diglycidyl ether of bisphenol and 3-glycidoxypropyltrimethoxysilane (GLYMO) and found a dependence of the conversion of epoxy groups and the degree of organic phase cross-linking on inorganic phase content. The high refractive indexed (RI) (1.505–1.867) transparent IOHR from triethoxysilane-caped poly(methyl methacrylate) and titanium as high refractive index component was also reported [9].

Besides the above, it is also known that the condensation of GLYMO and DPSD in the presence of titanium(IV)-isopropylate as a catalyst produced silica-based transparent epoxysilane resins. The effect of solvent, temperature and catalyst on the reaction products was shown by Wipfelder and Hohn in detail [10]. The condensation reaction of methoxy groups of MPTS with silanol groups of DPSD in the presence of Ba(OH)$_2$ as a catalyst is well studied [1,7]. The incorporation of third precursor by involving the same reaction pattern can change the hybrid properties like refractive index, optical property, etc. as already reported [11] in the MPTS and DPSD system. Here, we have chosen GLYMO instead of MPTS. As MPTS and GLYMO have methacrylate and glycidoxypropyl groups directly attached to silicon in addition to the three methoxy groups, the condensation reaction of GLYMO with DPSD in presence of Ba(OH)$_2$ will follow the same reaction procedure [1]. It is important to mention that the characteristics of the hybrid also depends upon the attachment of non-reactive organic groups such as alkyl or phenyl to silicon [1,2,7]. We have chosen phenyltrimethoxysilane (PTS) as the third precursor to verify the hybrid characteristics as an additional non-reactive organic group in the IOHR preparation.

In the present work, IOHR were synthesized from GLYMO, DPSD and PTS system using Ba(OH)$_2$ as a catalyst by non-hydrolytic sol–gel process which seems not studied earlier by following the reaction scheme as given in [7,11], already reported in MPTS, DPSD and HFT system. This was an initial part of our main study to explore the possibility of synthesizing silicon-based sol–gel resin by using some common precursors to be used as an encapsulate in optoelectronic devices such as white light emitting diodes (white LEDs) and photovoltaic cells, which may basically needs the resin with good refractive index, visible transparency as well as thermal stability. In this paper, we emphasized the condensation/polymerization, thermal stability, optical property of the IOHR-derived films as a function of compositions.

2. Experimental procedure

2.1. Preparation of IOHR

3-(Glydoxypropyl)trimethoxysilane (GLYMO, 98%), diphenylsilanediol (DPSD, 95%) phenyltrimethoxysilane (PTS, 97%), barium hydroxide (Ba(OH)$_2$, 95%) purchased from Aldrich were used as received. Toluene was used from Fisher Scientific (HPLC grade). The resins were prepared using requisite amount of precursors and Ba(OH)$_2$, as a catalyst (0.10–0.15 mol% to the total silane compound) to promote the condensation reaction between the precursors. In all the compositions, PTS content was kept fixed (20 mol%) while that of DPSD changed from 40 to 60 mol%, so that the total mol% of GLYMO and DPSD was 80 in each composition.

The preparation of the resins was made following the reaction scheme as given in Fig. 1. In one neck round bottom (RB) flask GLYMO and PTS are taken and stirred well for 5 min after tightly closing the mouth with rubber cork. The RB was then placed into 90 °C silicon oil-bath and barium hydroxide was then added. After 30 min, small amount (0.5–0.70 g) of DPSD was added in every 4–6 min intervals to prevent self-condensation and phase separation of DPSD. Vigorous evolution of methanol was observed and whole liquid mixture became clear during the reaction after 45 min and at that time addition of DPSD should be controlled to avoid excessive expulsion of methanol vapor. After complete addition of DPSD, the RB was kept at 90 °C for further 2 h to progress the reaction and then cooled it down to room temperature. It was mixed with toluene (1:0.5, v/v and stirred for 30 min at room temperature. The liquid was then filtered using 0.45 μm-size Whatman polytetrafluoroethylene (PTFE) syringe filter to remove the barium hydroxide particles. After that the by-product methanol as well as toluene was evaporated at 70 °C for 3 h by vacuum evaporator. The IOHR at all the compositions was oily transparent liquid, miscible with various organic solvents like toluene, cyclohexanone, chloroform, tetrahydrofuran, etc. and also in commercial epoxy resins but immiscible with water. The color of the resin was pale yellow, which lightened with increasing DPSD content. The liquid resins having 40–50 mol% of DPSD were storable.

2.2. Preparation of IOHR films

Thermal curing behavior without using thermal initiator of resins was studied by making thick films using resins with appropriate amount of toluene on cleaned silicon wafer and quartz glass substrates by a single spin coating (M–J Technics Co., SPIN COATER/SP-3000) at 2000 rpm for 20 s. The thickness of the coating film was maintained at ∼10 μm in each composition. Refractive indices, film thicknesses, and UV–vis transparency were measured from the coated films. The coated samples were

Fig. 1. The reaction scheme for the synthesis of IOHR.

air dried at 120 °C for 1 h and then baked at 200, 220 and 230 °C (±5 °C) for 3 h at each temperature in air atmosphere.

2.3. Characterizations

A Bruker, DPX 300 NMR (Nuclear Magnetic Resonance) instrument was used to measure ^{29}Si NMR spectra at 300 K of the resin taking 50 volume percent of liquid resin in CDCl$_3$ in presence of chromium(III) (Aldrich, 99.99%) acetylacetonate (30 mg L^{-1}) as a relaxation agent of silicon. TMS was used as a reference. Viscosity of the methanol-evaporated resins was measured by Brookfield digital viscometer (DVII) at 25 °C. The Fourier transform infrared (FTIR) spectra of the liquid resins and resin films made on silicon were recorded using Bio-Rad Win-IR (FTS-165) at 64 numbers of scans in 4000–400 cm^{-1} wavenumber region. Thermogravimetric analysis (TGA) were performed on a TA Instruments SDT 2960 (simultaneous DTA-TGA) with a heating rate of 10 °C min^{-1} in nitrogen atmosphere (flow rate of 100 cm^3 min^{-1}) up to 800 °C. The thermal behaviors of IOHR were carried out using differential scanning calorimeter (DSC) "TA Instruments DSC 2910" up to 300 °C in nitrogen atmosphere with a gas flow rate of 50 cm^3 min^{-1}. The DSC pan was loaded with 7–10 mg of IOHR sample. The weight average molecular weight of the liquid resins dissolved in tehrahydrofuran (THF) as an eluent was determined to verify the trend of molecular weight change with DPSD content by gel permeation chromatograms (GPC) using Alliance Waters 2690 separations module and 410 channels were used in 40 min run time for all the samples. The instrument was calibrated using polystyrene standards. Film thickness of the resin films were measured by field emission scanning electron microscopy (FESEM) (JEOL, JSM 6700F). A Prism Coupler (SAA-4000, Sairon Technology Inc.) was used to measure the refractive indices of the resin films at 632.8, 830, 1310 and 1550 nm laser beams. Ultraviolet–visible (UV–vis) spectra of the coated films on quartz glass were recorded by Shimadzu (UV-2550) UV–vis spectrophotometer.

3. Results and discussion

3.1. Characteristics of liquid IOHR

The ^{29}Si NMR is an effective tool to confirm the polycondensation reaction of silicon-based precursors. Therefore, the liquid IOHR were analyzed by ^{29}Si NMR to confirm the polycondensations. The NMR spectroscopic designation of Si atom are as follows: D^n and T^n denote the silicon from DPSD and combined GLYMO and PTS, respectively where superscript n indicates the number of siloxane bonds of the silicon. The details of the chemical shift appeared corresponding to the species [12] are given in Fig. 2 and Table 1. No D^0 species of diphenyldimethoxysilane (−29 ppm) which formed [1] through esterification of DPSD and methanol was noticed in all the resin compositions which possibly removed by vacuum heating at relatively higher temperature (70 °C). The formation of T^1, T^2 and T^3 species indicates that polycondensation reaction between the precursors was occurred efficiently in the resins forming the polysiloxanes, but the degree of condensation could not be understood.

It is possible to control the degree of the condensation reaction of the IOHR by changing their molar proportions, which directly affect the thermal and optical properties of the resins [1,2,5,11]. Furthermore, the modification of composition will lead to change rheological character, i.e. viscosity of the resin. In the application of the IOHR by blending with commercial epoxy resin or phosphor powder, it is necessary to know the viscosity of the IOHR. Fig. 3(a) plots viscosity change as a function of composition. The viscosity increases from 560 to 985 cps with increasing DPSD content from 40 to 50 mol%, and the viscosity of the IOHR at 60 mol% DPSD could not measured at room temperature because it was so viscous that the range of viscosity limit was beyond the viscometer. The very high viscosity at 60 mol% DPSD content clearly indicates the further condensation taking place between the precursors, and as a result the molecular weight of the IOHR may be increased. The abrupt increase of viscosity at 60 mol% of DPSD may be explained by its high degree of polymerization forming higher molecular weight polysiloxane, which needs to determine the molecular weight of the IOHR for its further verification.

The polycondensation between the precursors was again proved by measurement of molecular weight of the IOHR. The change of W_m as a function of composition is shown in Fig. 3(b). The weight average molecular weight (W_m) of the liquid IOHR with changing the composition was measured by GPC. The measured W_m shows

Fig. 2. ^{29}Si NMR of liquid IOHR of various compositions: (a) 40 mol%, (b) 50 mol%, and (c) 60 mol% DPSD. Detailed assignment of the signals is listed in Table 1.

Table 1
Assignment of species with their corresponding chemical shifts of silicon depending upon its bond states

Assignment of species	Chemical shifts (ppm)	Structural assignment
D^1	−36	
D^2	−43 to −45	
T^1	−48 to −54	
T^2	−56 to −61	
T^3	−65 to −70	
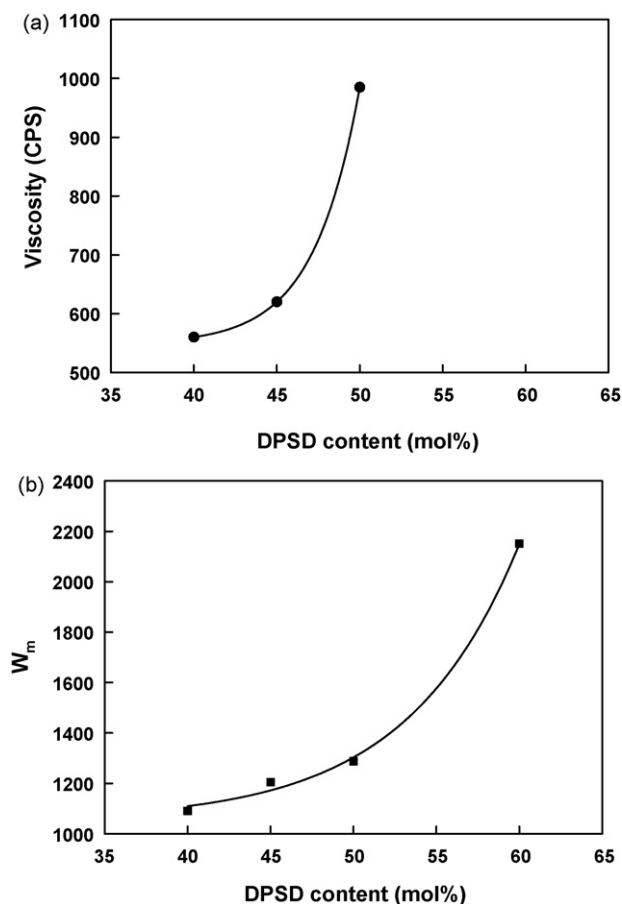
Fig. 3. Change of (a) viscosity and (b) W_m as a function of IOHR compositions.

Fig. 4. FTIR spectra of liquid IOHR.

that up to 50 mol% of DPSD, the W_m increased slowly within the range 1091–1288 but at 60 mol% it increased abruptly to 2151. It seemed that up to 50 mol% of DPSD the main molecular structure of the IOHR expected within pentamer to hexamer since the average molecular weight of the precursors is ∼215. However, in the case of 60 mol%, it increased to 2151 where decamer formation was possible due to further condensation reaction [7,11]. Without further verification, it was very difficult to remark on the structure of IOHR. However, it may be stated that up to 50 mol% of DPSD it was linear or cyclic. In case of 60 mol% of DPSD content, it was favored to be branched oligosiloxane due to the stoichiometry, which resulted in a high viscosity as well as molecular weight of the IOHR, as observed in MPTS and DPSD system [11]. The polycondensation reaction between the precursors was proved by NMR analysis, and viscosity and molecular weight determinations of the IOHR.

At the same time, it was necessary whether the epoxy group of the resins was stable or not from FTIR spectroscopy, which could be much effective to give the clear information in the matter [10]. Fig. 4 shows FTIR spectra of liquid resins with different compositions. In FTIR spectra of all the IOHR, the peak appeared at 910 cm^{-1} was the characteristic vibrations of epoxy ring, which indicates that during synthesis epoxy ring was not opened [10,13]. The peak at 816 cm^{-1} appeared in 40 mol% DPSD content resin, assigned as bending vibration of Si—O—Si bonds, and shifted towards lower frequency at 792 cm^{-1} in 60 mol% DPSD may be due to an overall decrease in the Si—O—Si bond angle [8,13]. It is interesting to note that the 1085 cm^{-1} (strongest peak) of resin having 40 mol% DPSD generated due to the vibration of v(Si—OCH$_3$) group gradually decreases its intensity and became unresolved at 60 mol% DPSD
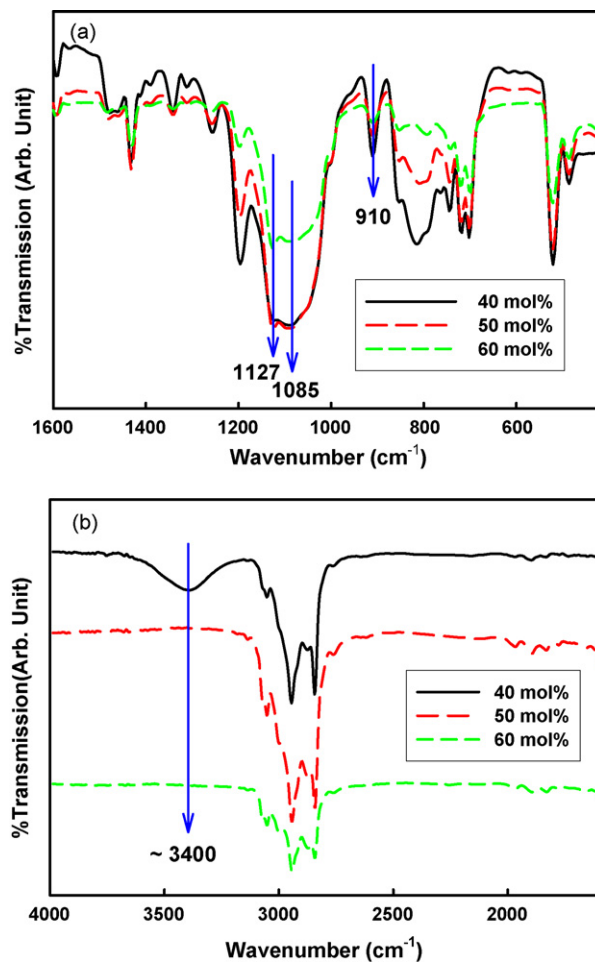
resin as compare to 1127 cm^{-1} vibration [10]. The strongest intensity vibration at 1085 cm^{-1} was also observed in GLYMO precursor. This was an indication that available —OCH$_3$ groups of precursors reacted with —OH groups of DPSD with increasing the later through this non-hydrolytic sol–gel condensation. The 1127 cm^{-1} vibration (not shifted) designated as v(SiC$_6$H$_5$) vibration increased with increasing DPSD content, due to the increasing phenyl groups. This vibration is also present (very strong) in DPSD precursor. In one IOHR composition, GLYMO:DPSD:PTS = 1:3:1 M proportion was chosen in such a way where equivalent numbers of —OH from DPSD and —OCH$_3$ from GLYMO and PTS were present. In this composition, we can consider that in one molecule of GLYMO and PTS, three numbers of —OCH$_3$ groups of total six was balanced with two numbers of —OH groups of each DPSD molecule of total six. Thus, theoretically if all the —OCH$_3$ and —OH groups are fully reacted generating methanol as a by-product, then the presence of unreacted —OCH$_3$ and —OH groups is not possible in this resin, but the appearance of broad and weak vibration at ∼3400 cm^{-1} indicate the presence of —OH groups in this resin which may be due to steric hindrance of bulkier phenyl groups blocked the —OH groups to react with —OCH$_3$ groups [14]. Here, up to 50 mol% DPSD in IOHR composition, the vibration for —OH groups was not observed which may be indicated that all —OH groups of DPSD reacted with the equivalent numbers —OCH$_3$ groups and excess unreacted number of —OCH$_3$ groups remained as Si—OCH$_3$ which showed the vibration at 1085 cm^{-1}. The decreasing intensity of ∼1085 cm^{-1} with increasing DPSD clearly indicates the further condensation of —OCH$_3$ groups

Table 2
Assignment of FTIR vibrations in the liquid IOHR

Vibrations (cm^{-1})	Assignment
488	Si—O—Si rocking vibration in LO mode
522	Lower frequency Si—O vibration
700, 720, 740	Various vibrations in ring bending modes of phenyl groups
1194	Si—O—Si asymmetric stretching vibration in TO mode
1430	Ring stretching vibration with some C—H bond bend coupling of phenyl groups
2950, 3051, 3072	ν(C—H) vibrations of C=C—H bonds of phenyl groups
2800–3000	Symmetric and asymmetric fundamental stretching vibrations of CH$_2$ and CH$_3$ groups

LO = longitudinal-optic and TO = transverse-optic modes.

Fig. 5. (a) TGA, (b) DTG and (c) DSC curves of various IOHR compositions.

with —OH groups of DPSD. In the case of 60 mol% DPSD content, the spectral region at ~1100–1000 cm^{-1} was broadened which also indicates the enhanced silica condensation [8] leads to high viscosity as well high molecular weight resin formation. In this region, the vibration due to ν(Si—OCH$_3$) was not clearly distinguished possibly a trace amount of unreacted Si—OCH$_3$ groups may be the present in the IOHR. It is true to mention here that the asymmetric stretching vibrations of Si—O—Si bridging sequences appeared in the range of 1260–1000 cm^{-1} in all the resin compositions and in our present study, some of the vibrations were immerged within the strong vibrations of Si—OCH$_3$ and SiC$_6$H$_5$ [14]. We were uncertain about the appearance of 1590 cm^{-1} vibration which may be responsible for epoxy group as reported in [10], but it was present in DPSD precursor. The presence of bridging sequences of Si—O—Si group was confirmed by asymmetric stretching vibration appeared at 1256 cm^{-1} in all the resin compositions. The combination of vibrations of the SiO$_2$ network was also observed in the regions of 1940–1640 cm^{-1} [14]. The other assignments of the FTIR vibrations are given in Table 2.

The application of the IOHR needs the investigation of thermal properties like thermal stability, or structural change during thermal curing. Thus, the thermal stability of the IOHR was studied by TGA/DTG, and any structural change or reactions was investigated by DSC. The weight loss as well as various pyrolysis steps up to 700 °C of various IOHR was shown in Fig. 5(a) and (b). It was seen that the weight loss and main pyrolysis steps of the various resins depends upon the DPSD content. In case of IOHR containing 40 mol% DPSD, the first pyrolysis step occurred at ~345 °C with a weak step at ~455 °C as well. The nature of the step changed again at 50 mol% of DPSD and one broad step 420 °C with nature of shoulder at ~345 °C. The abrupt change occurred at 60 mol% where most prominent step at 455 °C was detected. In our present study, with increasing DPSD content due to further condensation as revealed by molecular weight and viscosity measurements (Fig. 3), the amount of —OCH$_3$ groups decreased and therefore, the thermal stability increased. The shifting of main pyrolysis steps towards higher temperature with increasing DPSD content thus indicated higher thermal stability of the resins which supported the observation of Wipfelder and Hohl [10] in 40 mol% GLYMO and 60 mol% DPSD-based epoxysilane resins. In FTIR spectrum of 60 mol% DPSD content resin, as seen in Fig. 4(a), the vibration of νSiOCH$_3$ group at 1085 cm^{-1} is not clearly detected and may be indicated the very less amount of —OCH$_3$ groups were present, and the resin thus showed the higher thermal stability. In the first main pyrolysis step at ~350 °C of 40 mol% DPSD content resin, the weight loss was very high (~29%) but in 60 mol% DPSD it was very low (3.5%) also supported the above proposition. It was calculated from the TGA curves that from 40 to 60 mol% DPSD content resins the weight loss
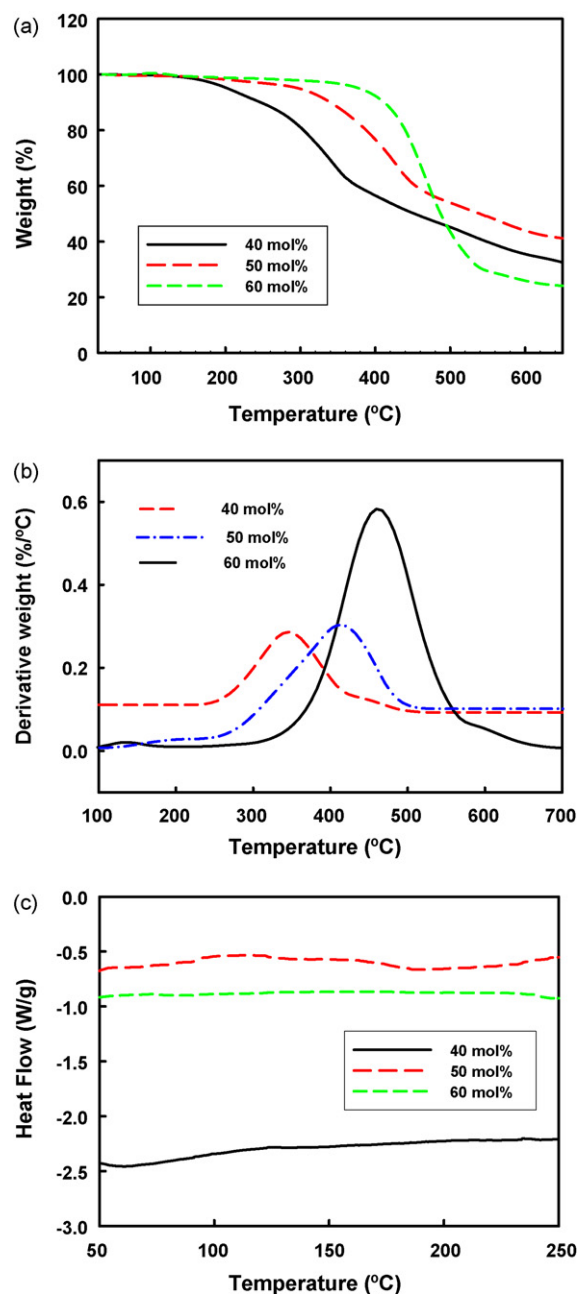
occurred within 7–1.4%, respectively at 230 °C, and no pyrolysis steps occurred below 300 °C. On the other hand, in DSC thermogram (Fig. 5(c)) of all the IOHR no exothermic and/or endothermic peaks were detected up to 250 °C, indicating that no reactions were taking place within this temperature range. Therefore, all the resins may be used up to 230 °C.

3.2. Characteristics of IOHR films

The curing behavior and optical properties of the IOHR at their various compositions were studied by making thick films on silicon wafer and quartz glass. FTIR spectroscopy is a useful tool to confirm the epoxide polymerization [10] of the IOHR. The FTIR spectra of the IOHR films baked at various temperatures were displayed in Fig. 6. The nature of spectra of all the thick films indepen-
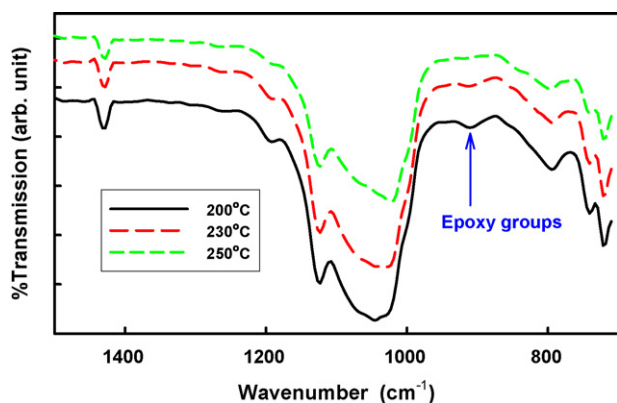
Fig. 6. FTIR spectra of 40 mol% DPSD content IOHR films on silicon wafer baked at various temperatures for 3 h at each temperature.

dent of DPSD content and so, here we have shown the spectra of 40 mol% DPSD content resin films baked at various temperatures. The epoxide vibration at $910 \, cm^{-1}$ nearly disappeared at $230 °C$ baking temperature but no vibration at $1106 \, cm^{-1}$ for glycol was detected indicating that the epoxide groups were polymerized without formation of glycol [8]. It also indicated that without using initiator thermal energy could able to polymerize the epoxy group. The presence of $1127 \, cm^{-1}$ vibration indicates the SiC_6H_5 group present in the films [10]. The vibration observed in the liquid resin at $1087 \, cm^{-1}$ decreased its intensity systematically with increasing baking temperature. The $1023 \, cm^{-1}$ vibration (strongest intensity) was resulted in the case of $230 °C$ baked resin film, and indicated that the Si–O–Si network was enhancing with the depletions of Si–OCH$_3$ groups.

It is well known that the film thickness varied with the viscosity of the resins. All the resins were diluted with toluene in such a way to get the film thickness $\sim$10 μm after curing the film at $230 °C$ for 3 h. The UV–vis transmittances (base-line corrected from same quartz glass slide) were shown in Fig. 7. In the spectra, the cut off wavelength remained within 260–270 nm and transmission observed through the entire visible region was above 90%. The fall of transmission below 350 nm may be due to presence of strong absorption band at $\sim$265 nm due to $\pi \rightarrow \pi^*$ transition of phenyl group.

Fig. 8 shows the refractive indices at various wavelengths of the IOHR films baked at $230 °C$ for 3 h as a function of DPSD content. The Lorentz–Lorentz equation as given below can give the refractive
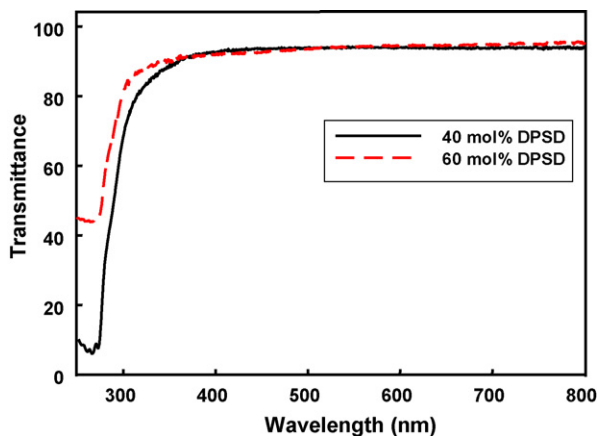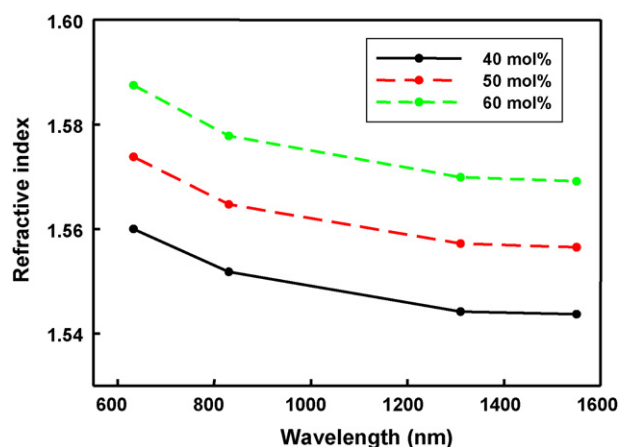

Fig. 8. Change of refractive index with wavelength of different composition of IOHR-coated films on silicon wafer baked at $230 °C$ for 3 h.

index change Δn by its differential form [15]

$$\Delta n = \frac{(n^2-1)(n^2+2)}{6n}\left(\frac{\Delta \alpha}{\alpha} + \frac{\Delta \rho}{\rho}\right)$$

where α and ρ denote polarizability and density, respectively.

From the plot it is seen that the refractive indices of the films at all the measured wavelengths increased with increasing DPSD content, which can be explained on the basis of higher electronic polarizability of the phenyl groups as well as densification of the IOHR films based on the above equation. A number of phenyl groups will be increased with increasing DPSD content, and epoxy groups are polymerized during thermal curing as observed by FTIR spectra (Fig. 6) of IOHR films baked within $200–230 °C$ for 3 h at each temperature. As the change of RI measured at 632.8 nm was 0.0063 on the densification of films, the increase of refractive index of the coatings with increasing DPSD is mainly due to the increasing phenyl groups [11].

4. Summary

Using barium hydroxide as a catalyst the condensation between GLYMO, DPSD and PTS produced new type of epoxysiloxane transparent IOHR only at $90 °C$. The thermal stability of the resins depended on DPSD content. It also controlled the viscosity as well variable molecular weight species formation in the resins. About 40–50 mol% DPSD content IOHR were storable but the resin at all compositions produced homogeneous solution with some organic solvents like THF, toluene, cyclohexanone, chloroform, etc. and easily miscible with commercial epoxy resins. No vibration at $3400–3500 \, cm^{-1}$ was detected up to 50 mol% of DPSD content resins and no reactions were observed up to $250 °C$ by DSC measurements. The IOHR synthesized were thermally curable at $230 °C$ without using initiator. The thick films ($\sim$10 μm) after curing produced optical transmission above 90% from 300 nm to entire visible region, and varied from 1.556 to 1.588 in refractive index at 632.8 nm, depending upon the composition especially on DPSD content. Therefore, the properties of the IOHR may demand its possible use in encapsulating commercial phosphor powder for white LEDs.

Fig. 7. UV–vis spectra of IOHR-coated films on quartz glass baked at $230 °C$ for 3 h.

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