

PREPARATION AND CHARACTERIZATION OF SILICA-POLYMER NANO HYBRID MATERIALS BY NON-HYDROLYTIC SOL-GEL PROCESS

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Methacryl- and epoxy-silica nano hybrid materials are synthesized from nanosized methacryl and epoxy grafted silica resin, and their physical properties are investigated. We found that their physical properties can be controlled by the variation of the precursor composition. They show low optical losses in NIR range for telecommunication (0.4 dB/cm @ 1310nm and 0.6 dB/cm @ 1550 nm), tunable refractive index (from 1.523 to 1.543 @ 1550nm), low birefringence (2×10^{-4}), linearity of dn/dT (2×10^{-4}) and thermally stable over 300°C, which are available for the optical applications.

(Key words : silica-polymer nano hybrid materials, absorption loss, tuneable refractive index, optical applications)

1. Introduction

Organic-inorganic nano hybrid materials (OINHM) have been investigated in composite materials fields since they can exhibit both inorganic and organic properties.^{1,2} The most important thing in the fabrication of OINHM is how to distribute inorganic and organic components homogeneously in nano scale since improvement and reproducibility of OINHM can be achieved through precise control of component size. In this regard, the employment of the nanosized organically grafted polysiloxane resin as a structuring unit can be one of the reliable processes for the fabrication of OINHM.^{3,4} Bulk or thick coating films of OINHM with homogeneous distribution of inorganic and organic components can be easily made from this nanosized resin since they are obtained just by polymerization of the functional organic groups in the resin.

Recently, non-hydrolytic sol-gel process have been received much attention for the fabrication of OINHM since nanosized organically grafted silica resins can be synthesized via this process. By a suitable selection of precursor molecules and optimization of processing parameters, many nanosized organically grafted silica resins can be synthesized with the consequence that silica-polymer nano hybrid materials with high homogeneity can be easily fabricated from these resins.^{5,6}

Diphenylsilanediol(DPSD) has silanol groups which can react with the alkoxy group of organo alkoxysilane to form siloxane bond, and 3-(trimethoxysilyl)propyl methacrylate (MPTS) and 3-glycidoxypropyltrimethoxysilane (GPTS) has a polymerizable methacryl and epoxy group. Therefore, nanosized organically grafted silica resins can be synthesized via condensation reaction between

silanol group of DPSD and these alkoxy silane, and then silica-polymer nano hybrid materials are obtained by polymerization of the functional organic groups in the resin.⁵⁻⁸

Thus, in the present study, we fabricated methacryl-silica nano hybrid materials from DPSD and MPTS, and epoxy-silica nano hybrid materials from DPSD and GPTS with various compositions. We also investigated the physical properties of these materials as a function of compositions for optical applications.

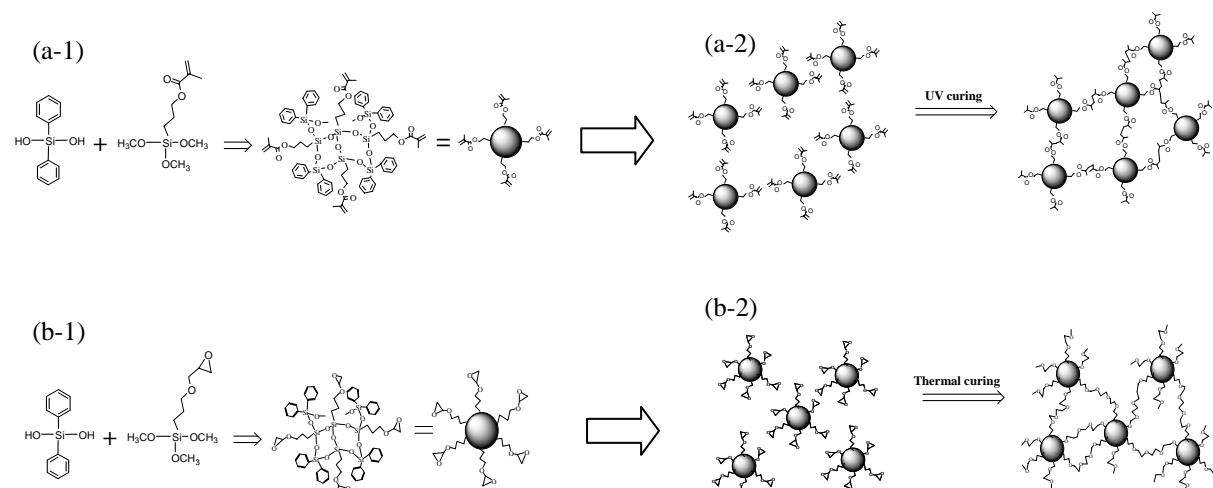


Fig. 1. Fabrication of silica-polymer nano hybrid materials

(a-1) Synthesis of methacryl grafted silica resin (MD resin) from MPTS and DPSD

(a-2) Fabrication of methacryl-silica nano hybrid materials from MD resins

(b-1) Synthesis of epoxy grafted silica resin (GD resin) from GPTS and DPSD

(b-2) Fabrication of epoxy-silica nano hybrid materials from GD resins

2. Experimental

The synthesis, characterization and instrumentation of the methacryl grafted and epoxy grafted polysiloxane resins are described elsewhere in detail.^{7,8}

Table 1. Formulation of silica-polymer nano-hybrid materials in the present study

| notation | MPTS (GPTS) | DPSD | Ba(OH) ₂ ·H ₂ O | mol % of DPSD |
|---------------|---------------|--------|---------------------------------------|---------------|
| MD 33 (GD 33) | 18.4g (17.5g) | 8.0g | 0.02g (0.04g) | 33.3 |
| MD 41 (GD 41) | 16.1g (17.5g) | 10.0 g | 0.02g (0.04g) | 41.7 |
| MD 50 (GD 50) | 13.8g (17.5g) | 12.0 g | 0.02g (0.04g) | 50 |
| MD 55 | 12.4g | 13.2 g | 0.02g | 55 |

NIR absorption spectra of the resin were obtained by UV/VIS/NIR spectrophotometer (Shimadzu UV-3101PC). Methacryl-silica nano hybrid coating films are fabricated from MD resin by the photopolymerization of methacryl groups using 2,2-Dimethoxy-2-phenyl-acetophenone (BDK,

Aldrich) as a photo-initiator. The concentration of BDK was 1 mol % of the methacryl groups and UV (500W Hg Lamp, ca 365nm, Oriel97453) doses were 860 mJ/cm² under nitrogen atmosphere. After photo-polymerization, the films were thermally treated at 150°C for 4 hrs. Epoxy-silica nano hybrid coating films are fabricated from GD resin by the thermal polymerization of epoxy groups using 1-methylimidazole (MI, Aldrich) as a thermal-initiator. The concentration of MI was 1 mol % of the epoxy groups and the films were cured at 150°C for 4 hrs. Refractive index and thermo-optic coefficient of these materials are measured using a prism coupler with a hot stage. Thermal stability of silica polymer nano hybrid materials was measured using TGA (TA, TGA 2050) under N₂ atmosphere.

3. Results and Discussions

We have already verified using ²⁹Si NMR spectroscopy and small angle neutron scattering that nanosized organically grafted silica resins in this study are successfully synthesized.^{7,8}

In order to confirm the suitability for the optical applications, NIR absorption characteristics were investigated. Fig. 1 and Fig. 2 show the NIR absorption spectra of the methacryl and epoxy grafted silica resins with various compositions, respectively. As shown in the NIR spectra, absorption coefficients of the resins at 850, 1310 and 1550nm are under 1dB/cm which are lower than the typical loss of optical PMMA whose absorption at 1550 nm is 1.5dB/cm.⁶ Thus, silica-polymer nano hybrid materials from these resins can be used for the optical applications. The NIR absorptions of the resins increase with DPSD contents since their particle sizes become larger due to the further condensation reaction, which makes the light scattering more severe.

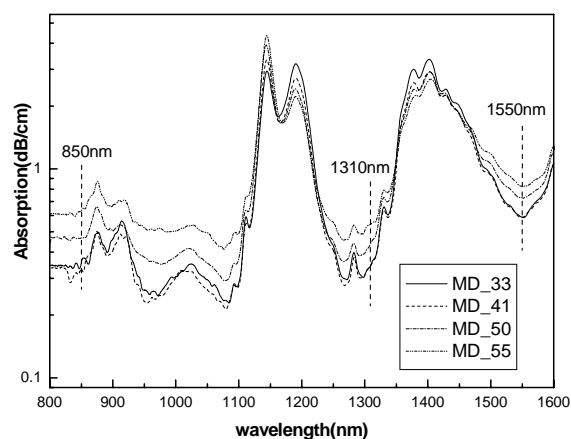


Fig. 1. NIR spectra of methacryl grafted silica resins

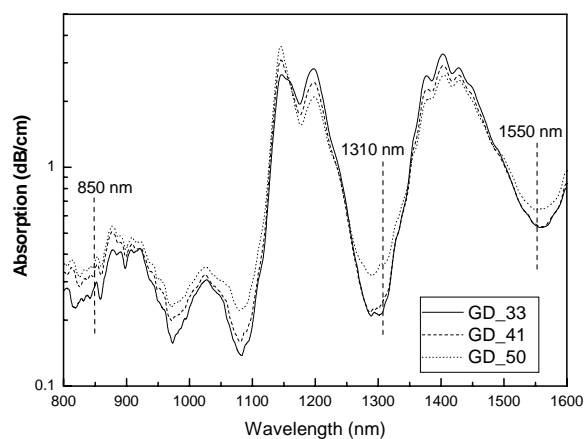


Fig. 2. NIR spectra of epoxy grafted silica resins

As previously mentioned, silica polymer nano hybrid materials can be obtained just by the polymerization of functional organic groups in the nanosized organically grafted silica resins. It was already found that BDK and MI are effective initiators for the polymerization of methacryl and epoxy groups (over 85 % of the conversion degree), respectively.^{9,10} Thus, using these initiators, silica-polymer nano hybrid coating films can be fabricated.

Fig. 3 and 4 show the refractive index (R.I) changes in silica-polymer nano hybrid coating films as a

function of compositions. As shown in these figures, R.I increases with DPSD contents due to the high polarizability of phenyl groups and further condensation reactions. R.Is of the epoxy-silica films are higher than those of methacryl-silica films under the condition of same DPSD contents. One of the plausible explanations of that is the polarity of the POE groups. POE groups produced by the polymerization of epoxy groups are more polar than methacryl groups. Therefore, R.I of the epoxy-silica films can be higher. Another possibility is the condensation reaction during the thermal curing. MI can act as a hydrolysis and condensation reaction catalyst between alkoxy group and silanol group produced via hydrolysis of alkoxy group and water in the air. As a result, epoxy-silica films are denser than methacryl-silica films and R.I of the epoxy-silica films are higher. As shown in the figures, all of the films show low birefringence (2×10^{-4}) and the refractive index can be tunable in the range of 2×10^{-2} and 1×10^{-2} for methacryl-silica and epoxy-silica nano hybrid materials, respectively. And we already found that the film thickness with very flat surface (under 1nm of RMS roughness) can be controlled from 10 to 100 μm without crack by changing the rpms and compositions.^{9, 10} It means that multi-mode optical waveguide as well as single mode waveguide can be fabricated with the same materials since core and clad materials can be obtained by the variation of the precursor compositions.

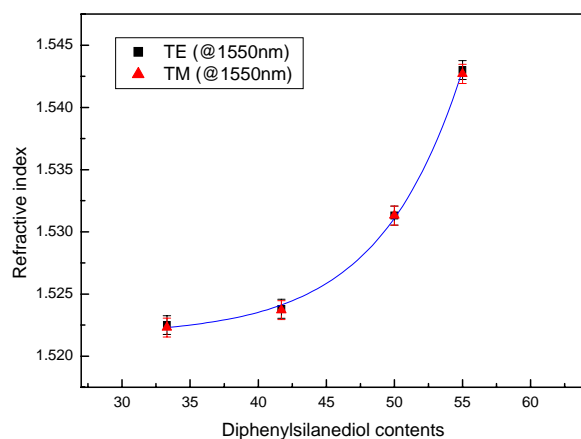


Fig. 3. R.I of methacryl-silica nano hybrid materials

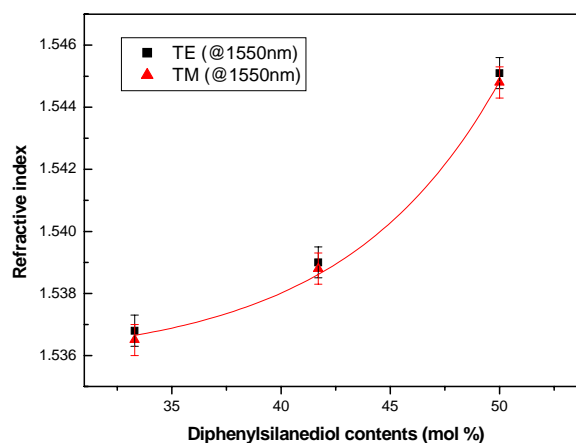


Fig. 4. R.I of POE-silica nano hybrid materials

Thermo-optic coefficient (dn/dT) of the films can be measured using a prism coupler with a hot stage.⁹⁻¹² Fig. 5 and 6 shows R.I changes of the silica polymer nano hybrid coating films as a function of temperature. As shown in the figures, the refractive index variations with temperature are in good linearity which is desired property for thermo-optical components. dn/dT of the films are almost same as 2×10^{-4} regardless of the compositions. Inorganic networks in the hybrid films increase with DPSD contents due to the further condensation reactions, which increase dn/dT . However, the particle size of the resin becomes larger with increasing DPSD contents and the methacryl or epoxy groups in the resin are sterically blocked by more phenyl groups. Thus, polymerization degree of these functional organic groups decreases with increasing DPSD contents, which decrease dn/dT . As a result, these two effects on dn/dT can be compensated mutually and dn/dT are same regardless of the compositions.

Table 2. shows the thermal stability of the silica polymer nano hybrid materials. As shown in the

table, the hybrid materials are thermally stable over 300°C. Since the organic components are covalently bonded with inorganic network in silica polymer nano hybrid materials, their thermal decomposition temperature can be elevated compared to that of typical organic polymer.

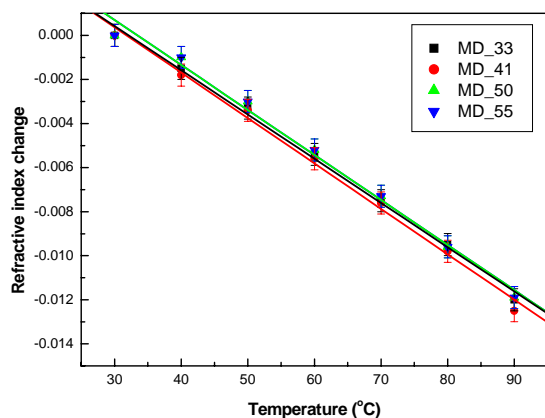


Fig. 5. R.I change of methacryl-silica nano hybrid materials

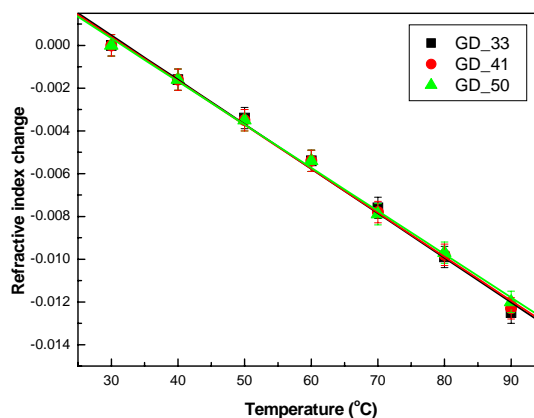


Fig. 6. R.I change of epoxy-silica nano hybrid materials

Table 2. Thermal stability of silica-polymer nano-hybrid materials

| composition | 5 wt % weight loss temperature |
|---------------|--------------------------------|
| MD 33 (GD 33) | 298 °C (353 °C) |
| MD 41 (GD 41) | 300 °C (350 °C) |
| MD 50 (GD 50) | 308 °C (363 °C) |
| MD 55 | 308 °C |

4. Conclusions

We have demonstrated the suitability of methacryl- and epoxy-silica nano hybrid materials from methacryl and epoxy grafted silica resins for the optical applications. They show low optical loss, tuneable refractive index change by variation of precursor composition, outstanding linearity of dn/dT in a wide range of temperatures and thermally stable over 300 °C, which mean these hybrid materials are good candidate for the optical applications.

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5. References

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