

Dispersion of silica nano-particles in sol-gel hybrid resins for fabrication of multi-scale hybrid nanocomposite

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Abstract Multi-scale hybrid nanocomposites containing both ~ 15 nm silica colloids and ~ 2 nm oligosiloxanes in a methacryl polymer matrix were newly designed and fabricated. Colloidal silica sols were dispersed in methacryl oligosiloxanes nano-hybrid resins synthesized by sol-gel reaction of methacryloxypropylmethoxysilane and diphenylsilanediol. On the basis of TEM and SANS analyses, it was confirmed that the silica colloids were compatibly dispersed and different sizes of colloidal silica and oligosiloxanes co-exist in the solutions. Multi-scale hybrid nanocomposites fabricated by UV and thermal curing with incorporation of silica colloids in the nano-hybrid materials show enhanced mechanical and thermal characteristics.

Keywords Multi-scale hybrid nanocomposites · Nano-hybrid · Sol-gel · Silica colloid · Dispersion · Small angle neutron scattering (SANS)

1 Introduction

With the current boom in nanotechnology, nanocomposites and nano-hybrids have received considerable attention as a new class of nanoscale materials [1–10]. The main goals of studying nanocomposites and nano-hybrids are to overcome the mechanical and thermal disadvantages of organic materials and the mechanical drawbacks of inorganic materials along with the realization of unique properties

that either material cannot provide alone. In the general scheme of nanocomposites or nano-hybrids, a nano-sized organic or inorganic phase is embedded or dispersed in a silica or polymer matrix. Since the nano-phase/matrix interface is continuous and homogeneous, favorable optical and electrical properties as well as mechanical and thermal properties can be generated without loss of transparency. In the classification system for organic-inorganic hybrid nanocomposites proposed by Sanchez et al. [11, 12], class I comprises nanocomposites with weak bonding between the organic and inorganic phases (van der Waals, hydrogen electrostatic bonding, hydrophilic-hydrophobic forces) fabricated by ex-situ physical mixing of the components. Class II comprises nano-hybrids with strong covalent or ionic-covalent bonding between the two phases synthesized by in-situ chemical routes using organo-metal compounds [13].

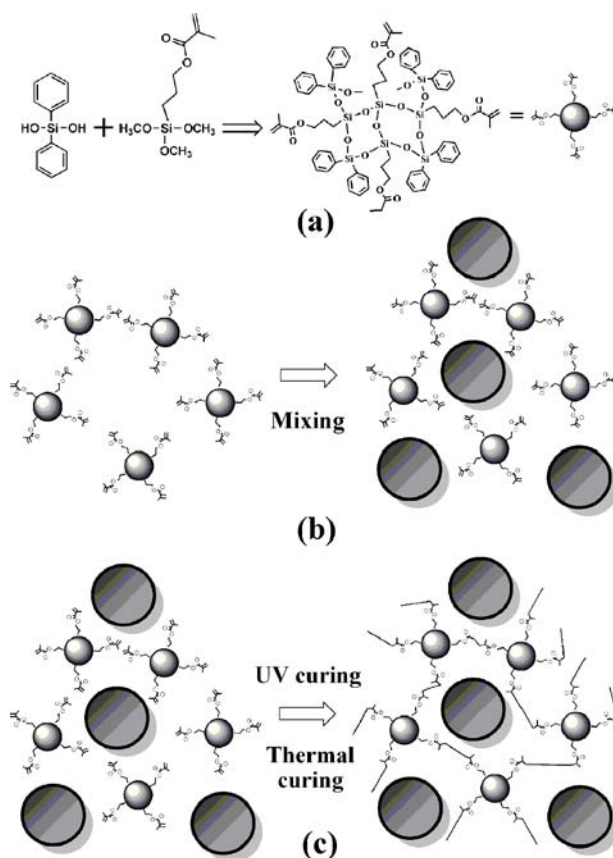
Examples of nanocomposites (class I) include sol-gel matrices embedded with organic dye and polymer matrices dispersed with nano-sized inorganic colloids or particles. For the polymer nanocomposites, pre-fabricated nano-sized (below 100 nm) colloids or particles are dispersed as a filler in the polymer matrix. These polymer nanocomposites show improved thermal and mechanical characteristics compared to matrix polymers. In the fabrication of these nanocomposites, dispersion of inorganic nano particles in the polymer resin is critical with respect to achieving the desired enhancement of thermal and mechanical characteristics. Agglomeration of inorganic nano particles in the polymer resin results in poor polymer-filler interaction and leads to degraded characteristics relative to those of the matrix polymer. Thus, to obtain effective dispersion of inorganic nano particles in the polymer resin, inorganic nano particle surfaces have been grafted with compatible organics with the matrix polymer or modified with dispersion agents in order to create electrostatic or steric forces [14].

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A sol-gel process using organo-alkoxysilane precursors is the simplest method to fabricate nano-hybrids (class II). Sol-gel reaction of organo-alkoxysilanes leads to the formation of nano-sized oligosiloxane clusters that can be grafted by polymerizable organics such as methacryl groups.[15–17] This simultaneous formation of organo-oligosiloxane provides a more reliable process for fabrication of nano-hybrids compared to nanocomposites. Following polymerization of organics, nano-hybrids are fabricated, wherein nano-sized (below 5 nm) oligosiloxanes are covalently bonded with the polymer matrix. Improvement and reproducibility of the nano-hybrids can be achieved through precise control of component species and amounts. The nano-hybrid is expected to be superior to the aforementioned nanocomposite since it is more homogeneous and has a continuous interface between the inorganic phase and organic matrix. However, the size of the oligosiloxanes synthesized by sol-gel reaction in the nano-hybrids is limited below 5 nm, and consequently significant enhancement of the characteristics is not obtained.

In order to realize a better design of hybrid nanocomposites with improved characteristics, a new type of multi-scale inorganic-organic hybrid nanocomposite integrating the concepts of nanocomposites and nano-hybrids is introduced here. Larger nano-sized (tens nm) particles are dispersed in nano-hybrid resins with smaller nano-sized (few nm) oligosiloxanes to fabricate multi-scale (tens and few nm sizes) hybrid nanocomposites. These multi-scale hybrid nanocomposites are expected to show considerably improved characteristics due to the compact assembly of silica particles and the capacity to control the sizes and dispersion of nano particles in the nano-hybrid resin.

Dispersion of nano particles in nano-hybrid resins is critical with respect to fabricating improved hybrid nanocomposites. In this study, we investigate the dispersion behavior of nano silica colloids in methacryl oligosiloxanes resin in the fabrication of methacryl hybrid nanocomposites containing multi-scale nano-sized silica phases (~ 15 nm silica particles and ~ 2 nm oligosiloxanes), as shown in Scheme 1. In previous studies, we synthesized nano-sized methacryl oligosiloxane resins using a solvent-free sol-gel reaction for fabrication of photo-curable methacryl nano-hybrids (Scheme 1(a)) [16–19]. Using small angle neutron scattering (SANS), it was found that the size of the synthesized methacryl oligosiloxanes is around 2 nm. We used colloidal methyl ethyl ketone (MEK)-based silica sol (MEKST, ~ 15 nm, Nissan Chemical Ind.) to disperse it in the methacryl nano-hybrid resins (Scheme 1 (b)). In the MEKST, the surface of the colloidal silica was hydrophobically modified with the CH_3 group for better dispersion in the organic matrix.[20, 21] Based on the dispersion of MEKST in methacryl nano-hybrid resins, transparent methacryl hybrid nanocomposites were fabricated by curing nano hybrid resins dispersed with silica nano



Scheme 1 (a) Synthesis of methacryl oligosiloxanes by condensation reaction of 3-methacryloxypropylmethoxysilane and diphenylsilanediol. (b) Dispersion of silica nano particles in methacryl nano-hybrid resin. (c) Fabrication of methacryl hybrid nanocomposites by curing of silica nano particle dispersed nano-hybrid resin

particles (Scheme 1(c)). The thermal properties of the fabricated methacryl hybrid nanocomposites were then characterized.

2 Experimental

2.1 Materials

2.1.1 Synthesis of methacryl nano-hybrid resin (Methacryl oligosiloxane, MD)

Methacryl-oligosiloxane was synthesized employing commercially available 3-methacryloxypropylmethoxysilane ($\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CO}_2(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$, MPTS, Aldrich) and diphenylsilanediol ($(\text{C}_6\text{H}_5)_2\text{Si}(\text{OH})_2$, DPSD, TCI) as starting precursors and barium hydroxide monohydrate ($\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$, Aldrich) as a catalyst to promote the condensation reaction among the precursors. No solvents such as methanol or water were employed as the synthesis proceeds by a solvent-free sol-gel method. MPTS and barium hydroxide mono-

hydrate powder were mixed and DPSD was subsequently added step by step for 2 hours to prevent self-condensation of DPSD and phase separation. The sol was stirred in a N_2 atmospheric vessel at $80^\circ C$ for 2 hours followed by the total addition of DPSD. Hence, the proportion of MPTS and DPSD was a 1:1 molar ratio and the catalyst was added in an amount of 0.1 mol% of total silicon atoms in the sol. The specific contents of materials were MPTS (13.78 g), DPSD (12 g), and catalyst (0.02g), respectively. After being filtered by a $0.45\mu m$ syringe filter, the methacryl nano hybrid resin (MD) was prepared.

2.1.2 Dispersion of colloidal silica nano particles in nano-hybrid resin (MS)

The prepared methacryl-oligosiloxane (MD) and methyl ethyl ketone ($CH_3COC_2H_5$, MEK) based colloidal silica sol (MEKST, Nissan Chemical Industries, 15nm, 30 wt% in MEK) were stirred in a flask at room temperature for 2 hours without further treatment. The amount of MEKST in the nano-hybrid resin was varied in order to compare the effect of colloidal silica particles. MS 10 and MS 20 were fabricated by adding 1g and 2g of MEKST to 10g of prepared MD, respectively. The total contents of silica in MS 10 and MS 20 were 0.3g (in total 11g) and 0.6g (in total 12g), respectively, over the hybrid nanocomposite.

2.1.3 Fabrication of multi-scale methacryl hybrid nanocomposite (MS hybrimer)

Multi-scale nano hybrid composite (MS hybrimer) coating films and bulks were respectively fabricated from the MS dispersion by UV-polymerization of methacryl groups using 2,2-Dimethoxy-2-phenyl-acetophenone ($C_6H_5COC(OCH_3)_2C_6H_5$, BDK, Aldrich) as a photoinitiator. The concentration of BDK was 1 wt% of methacryl-oligosiloxane (MD) and UV (500 W Hg Lamp, ~ 365 nm, Oriel97453) doses were 860 mJ/cm² under nitrogen atmosphere. After UV-polymerization, the films and bulks were cured thermally at $180^\circ C$ for 4 h.

2.2 Characterization

The particle and dispersion behavior of silica in methacryl-oligosiloxane (MS solution) was measured using Small Angle Neutron Scattering (SANS, HANARO at KAERI in Korea) [22]. The SANS measurement conditions were as follows: dilution with Acetone- d_6 (CD_3COCD_3 , Aldrich) in a 2 mm quartz cell; a 5.08 Å monochromatized neutron beam; and 2 and 3 m sample-to-detector distance to cover a Q range from 0.01 to 0.4 Å⁻¹. Q is the magnitude of the scattering vector and $Q = (4\pi/\lambda)\sin(\theta/2)$, where λ is the neutron wavelength and θ is the scattering angle. The scat-

tering was isotropic; therefore, the primary two-dimensional spectra were circularly averaged. All the correcting procedures were done with an IGOR program [23]. Transmission Electron Microscopy (TEM, JEM 3010 of JEOL, LaB₆ filament, 300 kV, 0.17 nm point resolution) and Dynamic Light Scattering (DLS, Brookhaven Instruments 90-plus, dilution with MEK, 658 nm, 90 degrees) were also employed for the particle dispersion analysis. Due to the compatibility of the solvent, the MS solution was blended with MEK.

The chemical structure change of the MS hybrimer was examined by FT-IR (JASCO FT-IR 680 plus, 4 cm⁻¹ resolution), before and after UV irradiation. Thermo-Gravimetric Analysis (TGA, SETRAM Setsys 16/18) of the MS hybrimer was performed under nitrogen flow at a heating rate of $5^\circ C/min$. Thermal mechanical properties of the MS hybrimer were tested via a Thermo-Mechanical Analysis (TMA, Seiko Instrument TMA/SS6000) under nitrogen flow at a heating rate of $5^\circ C/min$. Mechanical properties of the MS hybrimer coating such as hardness and elastic modulus were evaluated using a nano indenter (MTS Nano Indenter XP)

3 Results and discussion

3.1 Dispersion of colloidal silica particles in nano-hybrid resin

Methacryl-oligosiloxane is formed by a simple condensation reaction between the silanol group of DPSD and the methoxy group of MPTS. It was previously confirmed that methacryl-oligosiloxane is formed to fabricate a photocurable methacryl nano-hybrid resin in an earlier study.[16] It was found that the molecular sizes of the synthesized oligosiloxanes varied around 2 nm through SANS and the MALDI-TOF analyses. The fabricated methacryl nano hybrid (MD) resin, which has a viscosity of about 500 cps, is stable in air and at room temperature. The resin was mixed with a commercially available colloidal silica sol (MEKST), whose size is around 15 nm, in MEK solvent for fabrication of a multi-scale hybrid nanocomposite (MS) solution. According to the manufacturer, the surface of the colloidal silica is modified with a hydrophobic CH_3 group. MEKST was mixed with MD resin at 10 and 20 wt% (MS10 and MS20, respectively) to fabricate multi-scale hybrid nanocomposites containing different colloidal silica contents. MS10 and MS20 hold 2.7 and 5.0 wt% colloidal silica over the total MS solution, respectively.

Figure 1 shows TEM images of MS10 and MS20 solutions indicating homogeneous dispersion of 15 nm colloidal silica in the solution. Silica colloids are not agglomerated and phase-separated even upon exposure of a high energy electron beam, i.e., 200 kV TEM. The MS20 solution has higher silica colloid density than the MS10 solution. We also

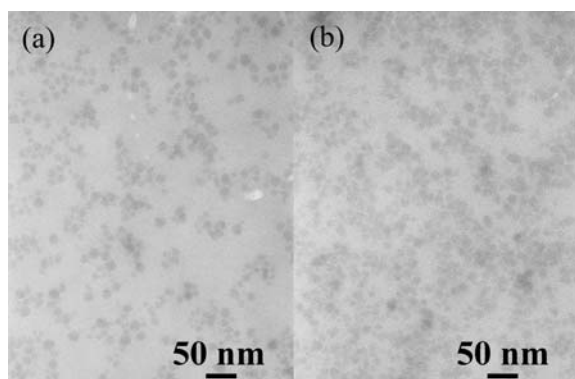


Fig. 1 TEM images of Multi-scale hybrid nanocomposite solution (MS solution), (a) MS 10 and (b) MS 20

mixed water and alcohol based colloidal silica sols with MD resin. However, the sols were not immiscible and the silica colloids were not dispersed, but instead agglomerated in the MD resin due to the resin's hydrophobic nature. On the other hand, MEKST is compatible with MD resin due to the hydrophobicity of MEK solvent. Hydrophobic CH_3 radicals grafted on the silica colloid surface lend a steric effect that prevents agglomeration in the methacryl environment of the MD resin. Thus, the silica colloids were well dispersed in the mixture of MEKST solution and MD resin, as shown in Fig. 1. Although the silica colloids are dispersed in the MS solution, oligosiloxanes cannot be observed in the TEM image. For fabrication of multi-scale hybrid nanocomposites using a MS solution, the co-existence of ~ 15 nm silica colloids and ~ 2 nm oligosiloxanes in MS solution should be verified. Thus, Small Angle Neutron Scattering (SANS) measurement, a very useful technique to characterize nano-sized moieties in materials, was carried out to confirm the molecular sizes of silica and siloxane in the MS solution. SANS measurements of MS10 and MS20 were made and compared with those of MEKST solution and MD resin. Fig. 2 presents whole plots of the scattered intensities obtained from the SANS data of the MS10 and MS20 solutions compared with those of MEKST solution and MD resin. The plots show double linear Guinier slopes in both low and high Q regions, revealing the particle size to be uniform. The slight variations in the entire regions in the 4 plots are caused by different sample-to-detector setups for the SANS experiment depending on the samples. The plots are curve fitted by simulation data using the program IGOR [23] to calculate the molecular sizes of the silica colloids and oligosiloxanes. The simulation data correspond well with the measurement data, as shown in Fig. 2. The simulations give the molecular sizes of the silica and oligosiloxanes in the solutions and resins, as presented in Table 1. As expected on the basis of a previous study and information, MD resin and MEKST solution contain homogeneous ~ 2.5 nm oligosiloxanes and ~ 14.7 nm silica colloids, respectively,

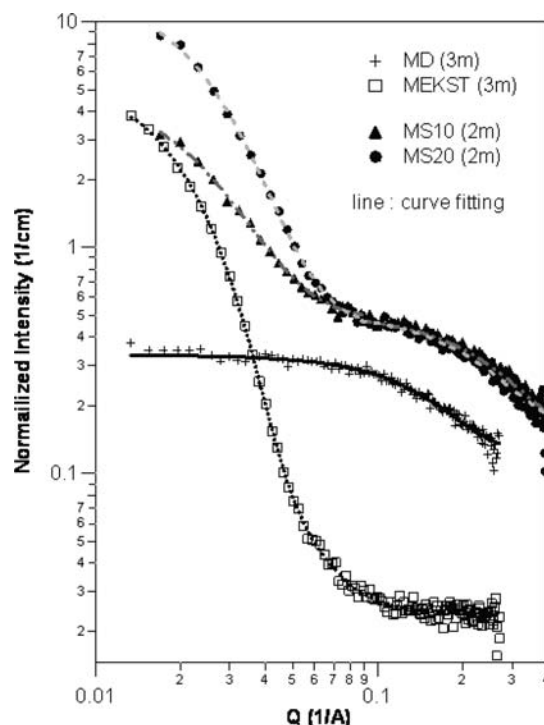


Fig. 2 Results of SANS experiment on the MS dispersion and results of curve fitting thereof

with low polydispersity. On the other hand, two distinct linear regions are found in the plots of the MS solutions, indicating the presence of two different sizes of particles. Scattering in the low Q region below 0.05 \AA^{-1} in the plots indicates the presence of large sized particles corresponding to silica colloids in the solution. This region provides information on the volume ratio of the silica colloids to the solvent as well as their size.

Comparing the plots of MEKST solution, MS solutions show a similar tendency in terms of scattered data. This reflects only a change in colloid content and no size variation. Each extrapolated intensity at $Q=0$ in plots indicates that the silica volumic content is abundant with high intensity value. On the other hand, the absence of size variation of

Table 1 Simulated particle size in multi-scale nano hybrid composite solution (MS solution)

Polyhardsphere		MD	MEKST
Radius (\AA)		12.3 ± 0.4	73.7 ± 0.9
Size (nm)		2.5 ± 0.1	14.7 ± 0.1
Polydispersity		0.17	0.29
Hardsphere		MS 10	MS 20
Low Q (silica)	Radius (\AA)	93.2 ± 1.9	93.8 ± 0.9
	size (nm)	18.6 ± 0.2	18.7 ± 0.2
High Q (oligosiloxane)	Radius (\AA)	10.4 ± 0.1	11.8 ± 0.1
	size (nm)	2.1 ± 0.1	2.4 ± 0.1

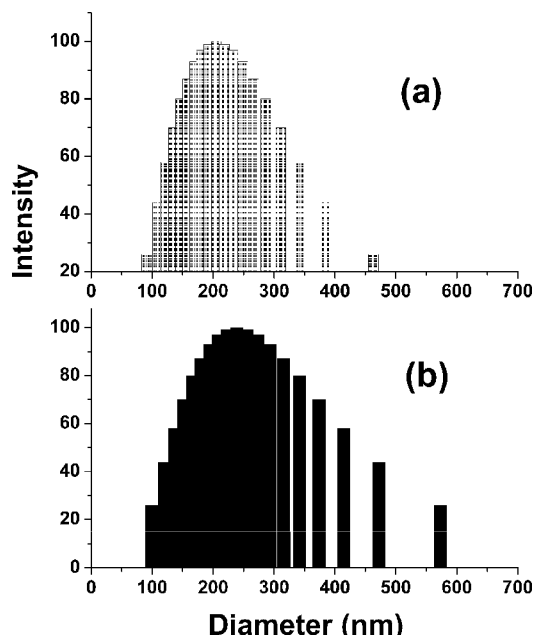


Fig. 3 Mass particle size distribution of multi-scale hybrid nanocomposite solution ((a) MS 10 and (b) MS 20) measured by DLS

silica particle results from the similar slope of the Guinier region, including the Q range corresponding to $QR_g = 1$ (R_g is the radius of gyration). These Guinier regions have only a few points such that their slopes cannot be measured directly, but instead are simulated indirectly from the whole curve. No size variation and the change in colloid content were confirmed by TEM image observations, as shown in Fig. 1. Another linear scattering region in the high Q region in the plots is formed by small sized particles corresponding to oligosiloxanes and the incoherent scattering factor of silica colloids. However, the incoherent factor of silica is negligible as compared with the plot of MD resin. Thus, this region dictates the size of the oligosiloxanes. Simulations of curve fitting were performed in separate linear regions of high Q and low Q areas in the MS solutions. Considering the volume ratio of MEKST solution to MD resin, the plots of the MS solutions are composed by combining plots of MEKST solution and MD resin. In Table 1, the simulated sizes of silica colloids and oligosiloxanes in MS solutions are listed and compared with those in MEKST solution and MD resin. The simulated values (18.6 nm and 18.7 nm) of silica colloid sizes in the MS solutions are larger than the values estimated from TEM and SANS. This is because the low Q region is affected by scattering of larger content oligosiloxanes in the high Q region. On the other hand, the simulated values of oligosiloxanes in the MS solutions are almost identical to those in MD resin. Therefore, it is ascertained that both large sized silica colloids and small sized oligosiloxanes exist together in the MS solutions, leading to the fabrication multi-scale hybrid nanocomposites.

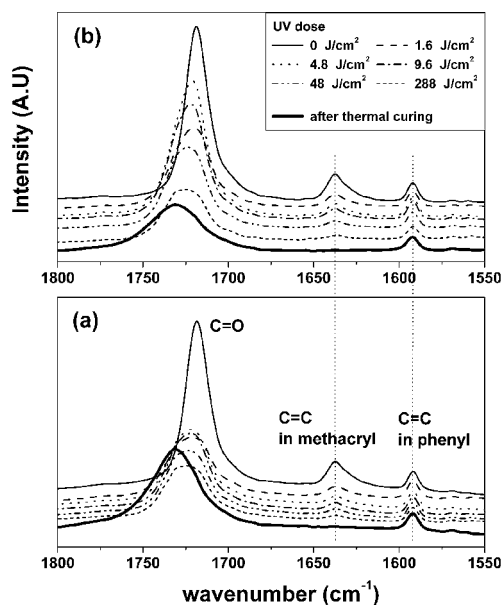


Fig. 4 C=C double bond change of methacryl group in multi-scale hybrid nanocomposite solution ((a) MS 10 and (b) MS 20) before and after UV irradiation.

Dynamic Light Scattering (DLS) was also employed to characterize the dispersion of the silica colloids in the solutions. Fig. 3 shows the mass particle size distributions of the MS solutions. Contrary to expectations formed on the basis of TEM images and SANS data, the dispersion of concurrently motioned particles in the MS solutions has a roughly 100 nm – 400 nm size distribution, regardless of silica colloid content. This may be due to the dynamic behavior of pseudo-clusters formed by interactions of silica colloids with oligosiloxanes in the solutions. Methyl grafted in silica colloids can bind with methacryl oligosiloxanes by hydrophobic interaction or van der Waals force to dynamically act as a pseudo-cluster [24–26]. It was found that dynamic light scattering is affected by the organic function of oligosiloxanes in hybrid nanocomposite solutions, causing different interaction with silica colloids [26]. Thus, DLS is not an appropriate method to characterize the size distribution of silica colloids and oligosiloxanes in hybrid nanocomposites solutions.

3.2 Fabrication of multi-scale hybrid nanocomposite by UV polymerization

MS solutions consisting of silica colloids in methacryl oligosiloxanes resin can be cured by UV polymerization of methacryl oligosiloxanes. Thus, the fabricated multi-scale hybrid nanocomposites show dispersed silica colloids and oligosiloxanes in methacryl polymer. UV polymerization of the methacryl group can be monitored by reduction of the FT-IR peak of the C=C double bond. Fig. 4 presents FT-IR spectra of MS10 and MS20 coated films on Si substrates as a function of UV dose. For both compositions, FT-IR peak in-

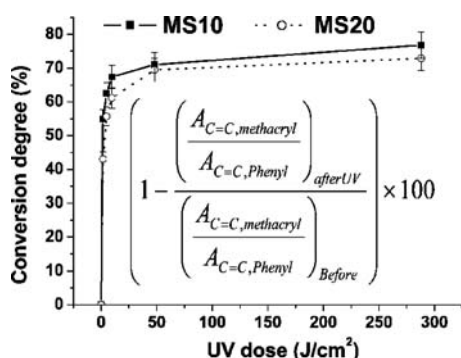


Fig. 5 Conversion degree of multi-scale hybrid nanocomposite solution (MS solution) with UV dose

tensity at 1720 cm^{-1} corresponding to the $\text{C}=\text{C}$ double bond in the methacryl group decreases with increasing UV dose, finally vanishing after thermal curing at 180°C . The conversion degree of the $\text{C}=\text{C}$ double bond in the methacryl group in comparison with the unvaried FT-IR peak at 1590 cm^{-1} of the $\text{C}=\text{C}$ double bond in phenyl group was calculated depending on UV dose, as shown in Fig. 5. It is shown that MS10 has a faster and slightly higher conversion degree than MS20. This is because more silica colloids screen the polymerization of methacryl radicals in the solution. However, the conversion degree, which indicates the extent of polymerization, reaches almost 75% for the solutions, a level high enough to cure both compositions. Despite the presence of silica colloids, the multi-scale hybrid nanocomposites were successfully fabricated by UV and thermal curing.

3.3 Characterization of multi-scale hybrid nanocomposites

First, the fabricated multi-scale hybrid nanocomposites are optically transparent despite incorporation of silica colloids. The hardness and elastic modulus of the fabricated multi-scale hybrid nanocomposites coated films (MS10 and MS20) were measured via nano-indentation and compared with a base methacryl oligosiloxanes nano-hybrid (MD) without

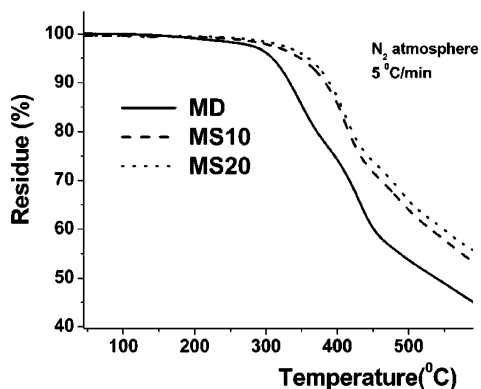
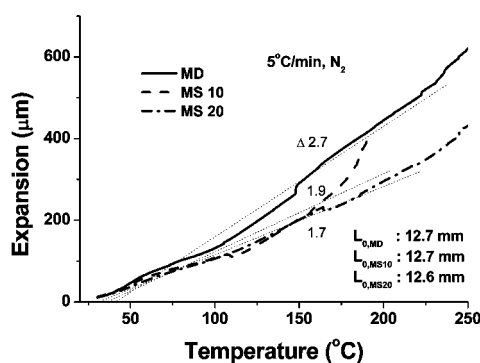


Fig. 6 TGA curves of methacryl-oligosiloxane (MD) and multi-scale hybrid nano composite (MS hybrimer)



	CTE ($\times 10^{-4}$)
MD	2.1
MS10	1.5
MS20	1.3

Fig. 7 TMA curves of methacryl-oligosiloxane (MD) and multi-scale hybrid nanocomposite (MS hybrimer) and calculated coefficient of thermal expansion thereof

silica colloids, as presented in Table 2. The coating hardness H_c was defined by the ratio of the maximum load and the contact area. The coating elastic modulus E_c was calculated on the basis of the initial slope of the unloading curve [27]. In this calculation, Poisson’s ratio of samples was assumed as 0.18 of silica. Both the hardness and elastic modulus of the multi-scale nanocomposites films are raised with increasing silica colloid content and are almost twice higher than those of nano-hybrid film for the same curing conditions. This suggests that the multi-scale hybrid nanocomposites with incorporation of silica colloids in the nano-hybrid offer improved mechanical characteristics, as expected. In addition, no cracking or chipping was observed during nano-indentation despite that the nanocomposites contain a large quantity of silica colloids.

Thermal characteristics of the fabricated multi-scale hybrid nanocomposites were also examined and compared with those of the base nano-hybrid. Fig. 6 presents thermal decomposition curves measured by TGA. The multi-scale hybrid nanocomposites show a 5 wt% weight loss temperature of roughly 350°C , exceeding that (310°C) of the base nano-hybrid at the same curing conditions. As found in general composites, embedment of silica colloids in a

Table 2 Nano-indentation hardness and elastic modulus of multi-scale hybrid nanocomposite (MS hybrimer)

	Hardness (H_c , MPa)	Elastic modulus (E_c , GPa)
MD	64 ± 5	2.3 ± 0.04
MS 10	194 ± 16	3.9 ± 0.23
MS 20	189 ± 10	4.0 ± 0.10

nano-hybrid plays a role of grabbing organic methacryl group, which results in a higher decomposition temperature. Also, although specimen preparation was difficult, thermal expansion of the samples was measured using TMA. Fig. 7 shows TMA curves of the fabricated multi-scale hybrid nanocomposites and that of the base nano-hybrid as well as their coefficients of thermal expansion (CTE). As expected in other composites, the CTE of the multi-scale hybrid nanocomposite is smaller than that of the base nano-hybrid and decreases with increasing silica colloid content. This is due to the addition of low thermal expansion silica colloids. Consequently, the mechanical and thermal characteristics were improved by incorporation of silica colloids in the nano-hybrid, as intended in the design of the multi-scale hybrid nanocomposites.

4 Conclusions

Colloidal silica sol in MEK solvent was dispersed in methacryl nano-hybrid resin to fabricate multi-scale hybrid nanocomposites. The size of the silica colloid is about 15nm and methacryl nano-hybrid resin synthesized by sol-gel reaction of MPTS and DPSD contains approximately 2nm oligosiloxanes. Thus, multi-scale hybrid nanocomposites consisting of silica colloids and oligosiloxanes together were successfully fabricated. Using TEM, it was confirmed that silica colloids were dispersed in the methacryl nano-hybrid resin. It was found that different sizes of silica colloids and oligosiloxanes co-exist in the dispersion solutions, as investigated by SANS. Thus, multi-scale hybrid nanocomposites having different size silica colloids and oligosiloxanes in a methacryl polymer matrix were fabricated by UV polymerization of the dispersion solution. It was found that the fabricated multi-scale nanocomposites have better mechanical properties, and higher thermal stability and lower CTE than a base nano-hybrid that does not incorporate silica colloids.

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References

- Schmidt H, Jonschker G, Goedicke S, Mennig M (2000) *J Sol-Gel Sci Technol* 19:39
- Sanchez C, Julian B, Belleville P, Popall M (2005) *J Mater Chem* 15:3559; Sanchez C, Lebeau B (2000) *MRS Bull* 26:377; Judeinstein P, Sanchez C (1996) *J Mater Chem* 6(4):511; Lecomte M, Viana B, Sanchez C (1991) *J Chim Phys* 88:39
- Haas KH (2000) *Adv Eng Mater* 2(9):571; Haas KH, Amberg-Schwab S, Rose K (1999) *Thin Solid Films* 351:198
- Gellermann C, Storch W, Wolter H (1997) *J Sol-Gel Sci Technol* 8:173
- Choi J, Kim SG, Laine RM (2004) *Macromol* 37:99
- Novak BM (1993) *Adv Mater* 5(6):422
- Reynaud E, Gauthier C, Perez J (1999) *Rev Metall/Cah Inf Tech* 96(2):169
- Chung HJ, Ohno K, Fukuda T, Composto RJ (2005) *Nano Letters* 5(10):1878
- Shaheen SE, Ginley DS, Jabbour GE (2005) *MRS Bull* 30:10
- Kim WS, Lee JH, Shin SY, Kim YC, Bae BS (2004) *IEEE Photon Technol Lett* 16(8):1888
- Sanchez C, Ribot F (1994) *New J Chem* 18:1007
- Sanchez C, Soler-Illia GJAA, Ribot F, Grosso D, Chimie CR 6:1131
- Schubert U, Husing N, Lorenz A (1995) *Chem Mater* 7:2010
- Schmidt H (1997) *J Sol-Gel Sci Technol* 8:557; Bourgeat-Lami E (2002) *J Nanosci Nanotech* 2:1; Haraguchi K, Usami Y (1997) *Chem Lett* 51:1997; Jun JB, Hong JK, Park JG, Suh KD (2003) *Macromol Chem Phys* 18:204
- Laine RM, Choi J, Lee I (2001) *Adv Mater* 13:800; Zhang C, Laine RM (1998) *J Am Chem Soc* 120:8380
- Eo YJ, Kim JH, Ko JH, Bae BS (2005) *J Mater Res* 20(2):401; Eo YJ, Lee TH, Kim SY, Kang JK, Han YS, Bae BS (2005) *J Polym Sci, Part B: Polym Phys* 43:827; Eo YJ, Kim JH, Ko JH, Bae BS (2004) *XX ICG'04 Proceedings* 20:11–046
- Lee TH, Kim JH, Ko JH, Bae BS (2004) *Mater Res Soc Symp Proc* 847:8.8.1–8.8.6; Lee TH, Kim JH, Bae BS (2006) *J Mater Chem* 16:1657; Kim WS, Kim KS, Eo YJ, Yoon KB, Bae BS (2005) *J Mater Chem* 15:465
- Hay JN, Raval HM (2001) *Chem Mater* 3396
- Schubert U, Husing N, Lorenz A (1995) *Chem Mater* 1010
- Yoshitake K, Yokoyama T (2000) *US Pat*, No 6 025 455
- Product information of MEK-ST, see <http://www.snowtex.com/>
- Seong BS, Han YS, Lee CH, Hong KP, Park KN, Kim HJ (2002) *Appl Phys A* 74(Suppl.):201
- NIST SANS homepage, see <http://www.ncnr.nist.gov/programs/sans/>
- Zhou Z, Wu P, Ma C (1990) *Colloids Surfaces* 50:177
- Arieh BN (1980) *In Hydrophobic interaction*, Plenum Press, New York and London, p 15
- Kim JH, Thesis MS (2005) Korea advanced institute of science and technology
- Oliver WC, Pharr GM (1992) *J Mater Res* 7:1564