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Spectroscopic analysis of methacrylate groups introduced on silica particle surfaces by the aza-Michael addition reaction

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Abstract−We modified silica nanoparticles with a N′-(3-trimethoxysilylpropyl)diethylenetriamine (TPDT) silane coupling agent, which has one primary and two secondary amino groups in each molecule, to introduce amino groups on silica surfaces. After surface modification of silica, we used an acrylate group containing 3-(acryloyloxy)-2-hydroxypropyl methacrylate (AHM) to introduce free radical polymerizable methacrylate groups by the aza-Michael addition reaction. Fourier transform infrared spectroscopy (FTIR), elemental analysis (EA), liquid state ^{1}H and ^{13}C nuclear magnetic resonance spectroscopy (NMR) and solid state cross polarization magic angle spinning (CP/MAS) ^{29}Si NMR were used to investigate the effects of various reaction conditions on the degree of reaction between the N-H groups of the TPDT-modified silica surface and the acrylate groups of AHM. We found that approximately 48% of the N-H groups of the TPDT-modified silica surface reacted with the acrylate groups of AHM, compared with approximately 83% of the N-H groups of pure TPDT reacting with the acrylate groups of AHM at the same reaction conditions. This lower degree of the aza-Michael addition reaction between the N-H groups of the TPDT grafted on the solid silica particle versus the N-H groups of pure TPDT, both with acrylate groups of liquid AHM, may be caused by the lower mobility of the N-H groups of the grafted TPDT on the solid silica particle and the higher steric hindrance caused by the solid silica particle.

Keywords: Silica, Silane Coupling Agent, Hydrolysis, Michael Addition Reaction, Methacrylate Groups

INTRODUCTION

There has been extensive research on the surface modification of silica nanoparticles, which can be used as fillers for nanocomposite, by using silanol groups on their surfaces [1,2]. In particular, to disperse hydrophilic silica particles uniformly into a hydrophobic organic polymer matrix, it is necessary to modify the surface of the silica particles to enhance their compatibility with organic polymers [3,4].

A 3-methacryloxypropyltrimethoxysilane (MPTMS) coupling agent has been widely used to introduce free radical polymerizable methacrylate groups onto silica surfaces. However, there is strong hydrogen bond formation between the C=O groups of methacrylate groups grafted on silica surfaces and the unreacted remaining Si-OH groups on silica due to the short linker length ($-CH_2)_n$-) of MPTMS (n=3). This hydrogen bonding formation restricts the movement of methacrylate groups and additional steric hindrance by solid silica particles cause the methacrylate groups grafted on silica exhibit lower reactivity [5].

To overcome this lowered reactivity, the distance between the C=O groups of the grafted methacrylate group and the remaining unreacted silanol groups on the silica surface requires lengthening. Therefore, we conducted silanization reactions using a secondary amino group containing bis[3-(trimethoxysilyl)propyl]amine (BTMA) and bis[3-trimethoxysilyl)propyl]ethylenediamine (BTPED) silane coupling agents with silica particles. After these reactions, we introduced methacrylate groups using secondary amino groups of silica surfaces by the aza-Michael addition reaction [6,7].

To graft more methacrylate groups on the silica surface, it was important to study the silanization reaction of silica particles with the (3-trimethoxysilylpropyl)diethylenetriamine (TPDT) silane coupling agent, which has one primary amino group and two secondary amino groups, totaling four N-H groups per TPDT molecule. After the silanization reaction, 3-(acryloyloxy)-2-hydroxypropyl methacrylate (AHM) was used to react with the grafted primary and secondary amino groups of TPDT on silica to introduce methacrylate groups by the aza-Michael addition reaction.

AHM, which was used to graft methacrylate groups, has one acrylate group that can undergo an aza-Michael addition-type reaction and one methacrylate group that does not undergo an aza-Michael addition reaction. Therefore, it is possible to introduce free radical polymerizable methacrylate groups on the silica surface using N-H groups of TPDT moiety at the TPDT-modified silica surface by the aza-Michael addition reaction.

The Michael addition reaction is one of the most widely used reactions to form C-C bonds in organic chemistry [8]. The aza-Michael addition reaction, which has nitrogen as a donor, can quickly form C-N bonds without a catalyst. It is known that secondary amino groups have stronger nucleophilic affinity than primary amino groups; therefore, secondary amino groups generally have more aza-Michael addition reactivity with a Michael acceptor than primary amino groups [9].

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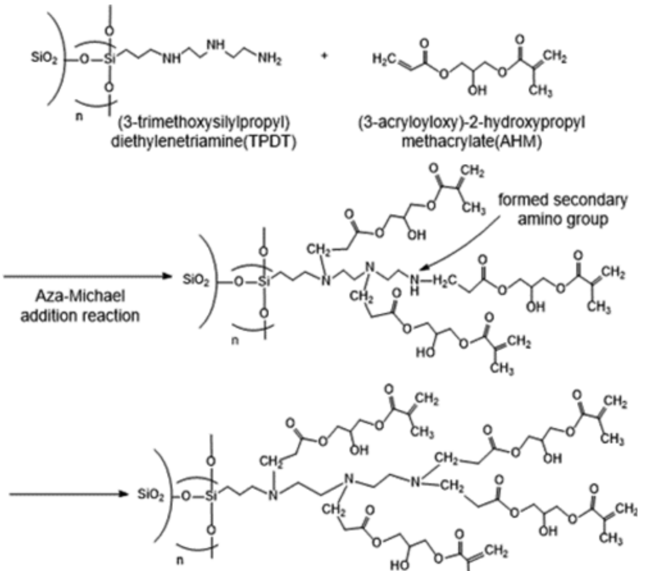

Fig. 1. Possible reaction schemes of AHM with amino groups on the TPDT-modified silica surface.

To efficiently introduce N-H groups on the silica surface by a TPDT silanization reaction, studies on the effect of reaction conditions such as pre-hydrolysis time, reaction time, reaction temperature and added TPDT/Si-OH molar ratios were thoroughly investigated. A better understanding of the aza-Michael addition reaction between TPDT-modified silica and AHM was achieved by changing the reaction time, changing the reaction temperature and varying the molar ratios of AHM to TPDT.

FTIR, EA, liquid state ^{1}H and ^{13}C NMR and solid state ^{29}Si NMR techniques were used to quantitatively analyze the effects of these reaction condition changes for the introduced amount of methacrylate groups on the silica surface. The modification process for silica nanoparticles with TPDT and AHM is schematically shown in Fig. 1.

EXPERIMENTAL SECTION

1. Materials

The silica Aerosil 200® (Evonik Degussa Corporation, average primary particle diameter 12 nm, surface area 200 m^2/g, 2.5 -OH/nm^2) used in this experiment was dried in a dryer at 150 °C for more than 3 h to remove the adsorbed water on the silica and cooled to room temperature in a desiccator. A mixed aqueous solution of ethanol (99.9% absolute, Duksan) and deionized water (MR-RU890, Mirae Sci. Corp., Korea) was used as a solvent. N′-(3-trimethoxysilylpropyl)diethylenetriamine (TPDT, 95%, Gelest) was used as a silane coupling agent, and 3-(acryloyloxy)-2-hydroxypropyl methacrylate (AHM, Aldrich) was used to introduce free radical polymerizable methacrylate groups onto the TPDT-modified silica surface. To prevent polymerization of the acrylate and methacrylate groups of AHM at 50 °C reaction, 0.1 wt% 2,6-di-*tert*-butyl-*p*-cresol (BHT, TCI) with respect to the AHM weight as a polymerization inhibitor was added. All reagents were used as-received without further purification.

2. Modification Reactions of Silica with TPDT

A total of 260 ml of ethanol and deionized water mixed in a 95 : 5 (v/v %) ratio was introduced into a 500-ml round-bottom flask. The flask was sealed with a glass stopper. The contents were then uniformly mixed with a magnetic stirrer at 300 rpm for 10 min. After mixing, 6.0 g pristine silica was added into a round-bottom flask and stirred for an additional 30 min. While stirring, 40 ml of an aqueous ethanol solution (95 : 5 v/v %) was added into another 60-ml HDPE bottle, and a specified amount of TPDT was added into the bottle and hydrolyzed for a period of time while being stirred.

The injection amount of TPDT was determined from the surface area of the silica particles and the silanol group density of the silica per nm^2 from the fact that each silicon molecule of the organosilane coupling agent usually forms one bond to the substrate surface [10]. Therefore, TPDT was injected at the following molar ratios into the HDPE bottle: TPDT/Si-OH=0.5 (0.66 g, 0.0025 mol), 1 (1.32 g, 0.0050 mol) and 2 (2.64 g, 0.0100 mol).

After the pre-hydrolysis reaction of TPDT for a specified stirring period, the pre-hydrolyzed TPDT was slowly added to the 500-ml round-bottom flask containing the dispersed silica particles; a silanization reaction was allowed while varying reaction time from 10 min, 30 min, 1 h, 2 h to 3 h with reaction temperature of 25 or 50 °C.

After the modification reaction was completed, the reaction mixture was filtered using a filter paper of 5-μm pore size (Advantec, Tokyo, Japan) under reduced pressure and was washed twice with aqueous ethanol solution (ethanol/deionized water=95/5 (v/v %). The sample was then washed with ethanol for three additional times. Then, the sample was dried for 2 h in a dryer at 50 °C and then dried again in a vacuum oven at 50 °C for 24 h.

3. Reaction of the TPDT-modified Silica with AHM

After the silanization reaction of TPDT with silica for 2 h with a TPDT/Si-OH=2 molar ratio, an aza-Michael addition reaction was carried out between the dispersed TPDT-modified silica with AHM by slowly adding AHM while stirring with a magnetic stirrer at 300 rpm and varying reaction time from 10 min, 30 min, 1 h, 2 h, 3 h to 5 h with reaction temperature of 25 or 50 °C.

Since TPDT molecules have four N-H groups per molecule, AHM was added for each 0.010 mol of TPDT-modified silica with varying molar ratios of AHM/TPDT=2 (4.28 g, 0.020 mol), 4 (8.56 g, 0.040 mol) and 8 (17.12 g, 0.080 mol). At the end of the reaction, the samples were purified in the same manner as the silica surface modification reaction with TPDT and with reduced pressure filtration.

4. Reaction of Neat TPDT with Neat AHM

To characterize the aza-Michael addition reaction products between the primary and secondary amino groups of TPDT with the acrylate groups of AHM, 0.005 mol (1.32 g) of TPDT was reacted with 0.020 mol (4.28 g) of AHM for 10 min to 5 h at 25 °C or 50 °C. Neat AHM was first placed in a 10-ml vial, and while stirring at 300 rpm with a magnetic stirrer, neat TPDT was added to react with the neat AHM.

For the aza-Michael addition reaction that was at 50 °C, 0.1 wt% of BHT was first dissolved in AHM to prevent polymerization of the acrylate and methacrylate groups of AHM. Then, TPDT was added to the AHM solution.

5. Characterization

To analyze the silica particles modified with TPDT and AHM, FTIR (Thermo, Nicolet is50), EA (Thermo Fisher/Flash 2000) and NMR (Bruker AVANCE 400WB) techniques were used.

FTIR spectra were measured by a transmission method using a sample pellet made of approximately 0.03 g of modified or pristine silica particles and scanned 32 times with a 4 cm^{-1} resolution in the range of 4,000 cm^{-1}-400 cm^{-1}. EA analysis measured the contents of C and N wt% in the sample. To analyze the effects of reaction time between the neat TPDT and the neat AHM, a small amount of sample was withdrawn and analyzed by ^{1}H and ^{13}C liquid state NMR in accordance with the reaction time using $CDCl_3$ as the solvent.

In addition, a quantitative analysis was conducted by integrating the area of a certain peak of the ^{1}H NMR spectrum using MestReC V4.8.6 (Mestrelab Research). For the solid state ^{29}Si NMR analysis, spectra were measured by the CP/MAS (cross-polarization/magic-angle spinning) method after TMS (tetramethylsilane) calibration using a 4-mm ZrO_2 rotor. A setting delay time of 3 s, a contact time of 2 ms, and spinning rate of 6 kHz were used.

RESULTS AND DISCUSSION

1. Effect of Pre-hydrolysis Time of TPDT

To investigate the effect of pre-hydrolysis time for TPDT, 0.66 g of TPDT to 10 ml of ethanol/deionized aqueous (95/5 v/v%) solution was added during stirring, and small samples were withdrawn at 10 min intervals from 0 min to 1 h and 20 min; the samples were dropped onto the diamond ATR (attenuated total reflection) crystal. Complete evaporation of the aqueous ethanol solution was permitted, and the FTIR spectrum was measured by the ATR method. For the quantitative analysis, the spectrum was transformed from the ATR mode to the transmission mode using the software in the FTIR spectrometer.

Fig. 2(a) is the FTIR spectrum of neat TPDT with peaks at 3,366, 3,297, 2,945, 2,839, 1,581, 1,464, 1,086 and 813 cm^{-1}. The peaks at 3,366 cm^{-1} and 3,297 cm^{-1} were caused by N-H stretching of the primary amino group, but the N-H stretching peaks of the secondary amino group are difficult to distinguish from the N-H stretching peak of the primary amino group at 3,297 cm^{-1} due to the overlap of those two stretching peaks [11,12]. The peak at 2,945 cm^{-1} is assigned from the asymmetric stretching of $SiOCH_3$ and the asymmetric stretching of CH_2 peak overlap; symmetric stretching of the $SiOCH_3$ and symmetric stretching of CH_2 peak overlapped at 2,839 cm^{-1}; the primary amino group bending vibration peak occurred at 1,581 cm^{-1}, and a CH_2 bending vibration peak appeared at 1,464 cm^{-1}. The bands at 1,086 cm^{-1} and 813 cm^{-1} resulted from $\equiv Si-O-CH_3$ asymmetric and stretching vibrations, respectively [13].

A comparison of Fig. 2(a) with Figs. 2(b) and (c), which are FTIR spectra of TPDT after hydrolysis for 10 min and 1 h and 20 min, illustrates that the intensity of the $\equiv Si-O-CH_3$ symmetric stretching peak of neat TPDT in Fig. 2(a), which appeared at 813 cm^{-1}, showed significantly reduced peak intensity in the hydrolyzed TPDT spectra in Figs. 2(b) and 2(c). Additionally, new peaks at 1,098 cm^{-1} and 1,050 cm^{-1} appeared in Figs. 2(b) and 2(c), each caused by $\equiv Si-O-Si\equiv$ and $\equiv Si-OH$, respectively, instead of the $\equiv Si-O-CH_3$ asymmetric stretching that appeared at 1,086 cm^{-1}.

The peak at 1,098 cm^{-1} was assigned to $\equiv Si-O-Si\equiv$ stretching formed by the self-condensation reaction between the hydrolyzed $\equiv Si-O-H$ groups of TPDT, and the peak at 1,050 cm^{-1} was assigned to the hydrolyzed $\equiv Si-OH$ stretching peak [13]. These results confirm the formation of a $\equiv Si-OH$ group by the hydrolysis of the $\equiv Si-O-CH_3$ of TPDT and the self-condensation reaction between the formed $\equiv Si-OH$ groups to form a $\equiv Si-O-Si\equiv$ bond. Thus, by increasing the hydrolysis time from 10 min to 1 h and 20 min, the intensity of the $\equiv Si-OH$ peak appearing at 1,050 cm^{-1} gradually decreased by the self-condensation reaction between $\equiv Si-OH$ groups, but the relative peak intensity of the $\equiv Si-O-Si\equiv$ bond at 1,098 cm^{-1} gradually increased from a shoulder peak in Fig. 2(b) to the sepa-

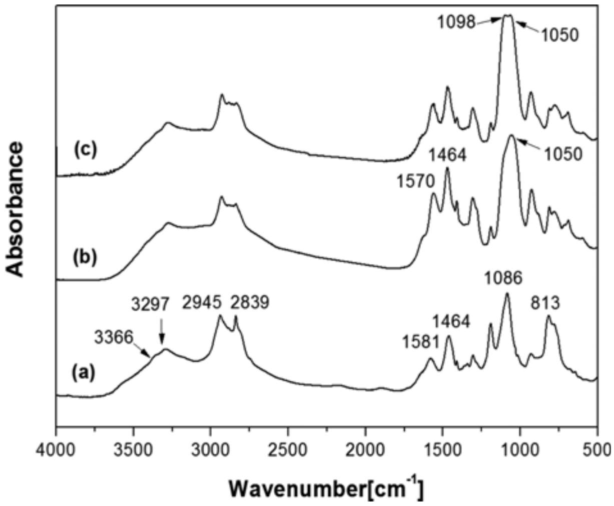

Fig. 2. FTIR spectra of (a) neat TPDT; (b) TPDT hydrolyzed for 10 min; (c) TPDT hydrolyzed for 1 h and 20 min.

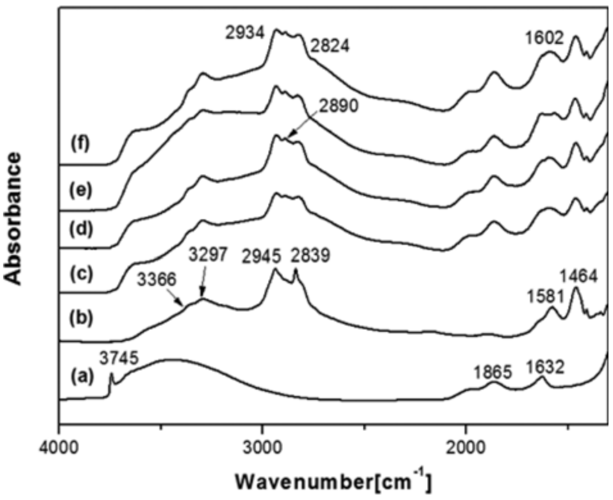

Fig. 3. FTIR spectra of (a) pristine silica; (b) neat TPDT; modified silica with (c) 0 min pre-hydrolyzed TPDT; (d) 20 min pre-hydrolyzed TPDT; (e) 40 min pre-hydrolyzed TPDT; (f) 1 h pre-hydrolyzed TPDT.

Table 1. FTIR peak area ratio changes with different pre-hydrolysis times

Sample	Area ($1,865\ cm^{-1}$)	Area ($1,602\ cm^{-1}$)	Area ($1,464\ cm^{-1}$)	Area ratio ($1,602\ cm^{-1}/1,865\ cm^{-1}$)	Area ratio ($1,464\ cm^{-1}/1,865\ cm^{-1}$)
Pristine silica	9.79	0	0	0	0
Neat TPDT	0	4.24	9.55	-	-
0 min Pre-hydrolyzed	7.43	4.06	4.91	0.55	0.66
20 min Pre-hydrolyzed	7.07	6.26	6.72	0.89	0.95
40 min Pre-hydrolyzed	5.25	4.21	4.52	0.80	0.86
1 h Pre-hydrolyzed	9.90	7.91	7.31	0.80	0.74

rate distinct peak in Fig. 2(c).

To determine the optimum pre-hydrolysis time of TPDT for the surface modification reaction of silica, silanization of silica with TPDT was performed by changing the pre-hydrolysis time of TPDT from 0 min, 20 min, 40 min and 1 h at 25 °C for 1 h reaction time; their FTIR spectra are shown in Fig. 3. FTIR spectra in Fig. 3 are plotted in 4,000-1,300 cm^{-1} region only, because a very strong broad Si-O-Si stretching peak of silica at 1,110 cm^{-1} overlaps with 1,098 and 1,050 cm^{-1} peaks.

The pristine silica spectrum shown in Fig. 3(a) has characteristic peaks at 3,745, 1,865 and 1,632 cm^{-1}. The peak at 3,745 cm^{-1} is due to the isolated silanol groups on the silica; the peak at 1,865 cm^{-1} is caused by the overtone band of silica; the peak at 1,632 cm^{-1} is -OH bending vibration of the H_2O adsorbed on the silica surface [14].

The spectrum of neat TPDT illustrated in Fig. 3(b) shows peaks at 3,366, 3,297, 2,945, 2,839, 1,581 and 1,464 cm^{-1}, and Figs. 3(c), (d), (e) and (f) show spectra of the modified silica with 0 min, 20 min, 40 min and 1 h pre-hydrolyzed TPDT. The figures show characteristic TPDT peaks at 2,934, 2,890, 2,824, 1,865, 1,602, and 1,464 cm^{-1}. Each peak represents asymmetric stretching of CH_2, symmetric stretching of CH_3, symmetric stretching of CH_2, overtone band of the silica, bending vibration of the primary amino group, and bending vibration of CH_2, respectively. Therefore, based on these results, it was possible to confirm the surface modification of silica by TPDT.

To quantitatively analyze the FTIR spectrum changes of modified silica treated with different time durations of pre-hydrolyzed TPDT, the peak area at 1,865 cm^{-1} was used as an internal reference because the peak intensity did not change even after the silica surface modification reaction. Then, changes in the peak area ratio (AR) were calculated for the primary amine bending vibration peak at 1,602 cm^{-1} and the CH_2 bending vibration peak at 1,464 cm^{-1} using the following Eq. (1). The calculated AR values are shown in Table 1 [15,16].

$$\text{Area Ratio (AR)}=(\text{Area of characteristic } cm^{-1} \text{ peak})/(\text{Area of } 1,865\ cm^{-1} \text{ peak}) \quad (1)$$

When the AR value results in Table 1 were compared, it was evident that the AR values for the 1,602 cm^{-1} peak changed from 0.55, 0.89, 0.80 and 0.80, and the AR values for the 1,464 cm^{-1} peak changed from 0.66, 0.95, 0.86 and 0.74 with increase in the pre-hydrolysis time for TPDT from 0 min, 20 min, 40 min and 1 h. The AR values for both peaks of pristine silica are 0.

The AR values increased for 0 min to 20 min pre-hydrolyzed TPDT-treated silica, but the AR values for the 40 min and 1 h pre-hydrolyzed TPDT-treated silica produced lower AR values than that of the 20 min pre-hydrolyzed TPDT-treated silica. These results confirmed that less TPDT moiety was introduced for the 40 min and 1 h pre-hydrolyzed TPDT-treated silica than for the 20 min pre-hydrolyzed TPDT-treated silica.

In conclusion, we confirmed a higher amount of TPDT moiety introduction for silica treated for 20 min, 40 min and 1 h pre-hydrolyzed TPDT than for the unhydrolyzed TPDT-treated silica. The highest amount of TPDT moiety introduction was also confirmed for the 20 min pre-hydrolyzed TPDT-treated silica than for the 0 min, 40 min and 1 h pre-hydrolyzed TPDT-treated silica.

When the pre-hydrolysis time was 40 min or 1 h, ≡Si-OH groups formed by ≡Si-O-CH_3 hydrolysis of TPDT underwent self-condensation reactions with the other ≡Si-OH groups to form a ≡Si-O-Si≡ bond, making colloidal particles, corresponding insoluble networks [17], since hydrolysis and self-condensation reaction of TPDT is very fast [18].

As a result, if pre-hydrolysis times are over 20 min, more oligomer forms of TPDT adsorb on the dispersed silica particles, which have a lower reactivity than that of the monomeric form of hydrolyzed TPDT.

2. Effect of Modification Time with TPDT

To investigate the effects of modification reaction time on the degree of silanization of silica particles for the fixed pre-hydrolysis time of TPDT at 20 min, the reaction times were triggered from 10 min, 30 min, 1 h, 2 h and 3 h, and the carbon and nitrogen content of the modified silica was measured by EA analysis (see Table 2).

As shown in Table 2, an increase in nitrogen content occurred with an increase in reaction time, from 1.89, 1.93, 1.94, 1.94 to 1.95%, and an increase in carbon content from 4.34, 4.49, 4.51, 4.53 to 4.53%.

Table 2. Nitrogen and carbon contents with different modification times

Sample	Nitrogen [%]	Carbon [%]
10 min Treated silica	1.89	4.34
30 min Treated silica	1.93	4.49
1 h Treated silica	1.94	4.51
2 h Treated silica	1.94	4.53
3 h Treated silica	1.95	4.53

Therefore, when the silica surface was modified with TPDT, CH_2 and the primary and secondary amino groups were introduced onto the silica surface, and the amount of TPDT moiety on the silica surface increased till 1 h reaction time and reached a saturation over 1 h.

As shown in Table 2, the TPDT moiety introduction rates were relatively fast until 30 min of reaction time, followed by a gradual increase after that period. Therefore, wes confirmed that most of the modification reaction was completed within a 2 h reaction period.

In addition, FTIR techniques were used to investigate the effects of reaction time on the modification degree of silica particles. Eq. (1) was used to calculate the AR values of the CH_2 bending vibration peak at 1,464 cm^{-1} while varying the reaction time to 10 min, 30 min, 1 h, 2 h and 3 h. The calculated AR values gradually increased from 0.54, 0.62, 0.66, 0.74 and 0.78, the same trend as found in the EA results, confirming that most of the modification reaction was completed with 2 h of reaction time. Therefore, a fixed reaction time of 2 h was used throughout the experiment to complete the modification reaction between TPDT and the silica particles.

3. Effect of the Input Molar Ratio of TPDT to Si-OH

To investigate the effect of the input molar ratio of TPDT to the silanol groups on the silica surface, molar ratios of TPDT/Si-OH= 0.5, 1.0 and 2.0 were used and reacted at a fixed temperature of 50 °C for 2 h. After the reaction, the FTIR spectra of modified silica were measured, as shown in Fig. 4.

Fig. 4(a) is the spectrum of pristine silica showing major peaks at 3,745, 1,865 and 1,632 cm^{-1}. Figs. 4(b), (c) and (d) are spectra of the modified silica with a TPDT/Si-OH molar ratio of 0.5, 1.0 and 2.0, respectively. It was confirmed that the silica surface was modified by observing peaks at 3,366, 3,297, 2,934, 2,890, 2,824 and 1,464 cm^{-1}, which are characteristic peaks of TPDT.

The gradual shift in the bending vibration peak of the primary amino group of TPDT was also found at 1,632 cm^{-1} to 1,602 cm^{-1}, and the broadening of this particular peak was shown in the FTIR spectra of TPDT-modified silica.

The peak that appears at 1,632 cm^{-1} is due to the -OH bending vibration of the H_2O adsorbed on the silica surface. When TPDT was grafted on the silica surface, the bending vibration peak of the primary amino group at 1,602 cm^{-1} overlapped with the bending vibration of the above -OH group at 1,632 cm^{-1}, forming a broad peak.

As a result, for the reaction of TPDT/Si-OH=0.5, the amount of grafted TPDT on the silica surface was small; therefore, the -OH bending vibration peak of the H_2O adsorbed on the silica appeared relatively stronger than expected. As the amount of reacted TPDT was increased, the grafted amount of TPDT on the silica surface increased as well, and the peak at 1,602 cm^{-1} appeared more strongly.

To quantitatively analyze the FTIR spectra variations of the modified silica with the molar ratio change of TPDT to the Si-OH groups of the silica, AR values using Eq. (1) for the isolated silanol peak at 3,745 cm^{-1}, the bending vibration peak of the primary amino group at 1,602 cm^{-1} and the bending vibration of CH_2 at 1,464 cm^{-1}, were calculated accordingly. As a result, the AR values for the 3,745 cm^{-1} peak were found to gradually decrease from 0.541 of pristine silica to 0.025, 0.006 and 0.004; the AR values for the 1,602 cm^{-1} peak of the pristine silica increased from 0 to 0.55, 0.68 and 0.74; the AR values for the 1,464 cm^{-1} peak increased from 0 to 0.57, 0.88 and 1.01. These results confirmed that the amount of grafted TPDT increased with an increase of the TPDT/Si-OH input molar ratio.

4. Effect of AHM/TPDT Molar Ratio

To study the effect of changing the molar ratios of AHM to TPDT used to modify silica particles, silica particles modified with a TPDT/Si-OH=2 molar ratios were used and reacted with varying molar ratios of AHM/TPDT (2, 4 and 8). The FTIR spectra of the resulting silica particles were measured, and the results are shown in Fig. 5.

Fig. 5(a) represents the spectrum of pure AHM, showing peaks at 3,488, 3,108, 3,041, 2,960, 2,931, 2,897, 1,722, 1,638 and 1,618 cm^{-1}. Each peak represents stretching of -OH, stretching of the $=CH_2$ of the methacrylate group, stretching of the $=CH_2$ of the acry-

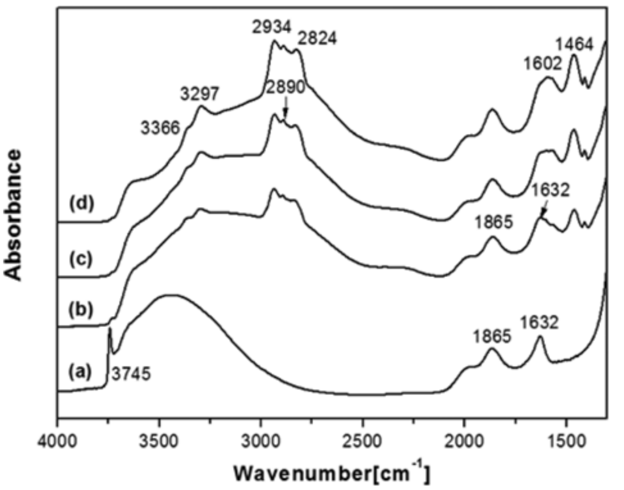

Fig. 4. FTIR spectra of (a) pristine silica; (b) modified silica with TPDT/Si-OH=0.5; (c) modified silica with TPDT/Si-OH=1; (d) modified silica with TPDT/Si-OH=2.

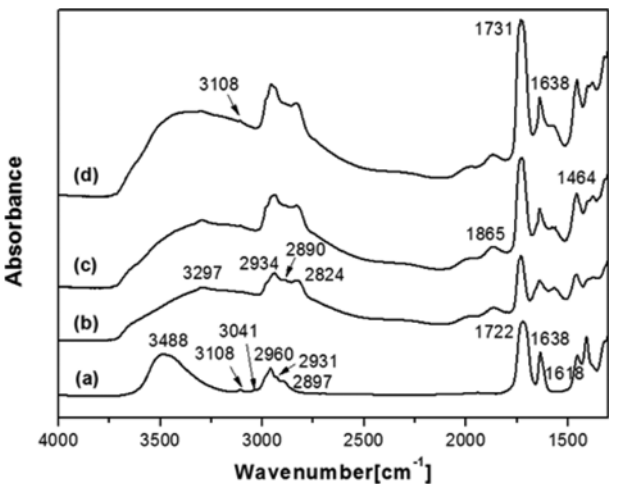

Fig. 5. FTIR spectra of (a) neat AHM; (b) modified silica with AHM/TPDT=2; (c) modified silica with AHM/TPDT=4; (d) modified silica with AHM/TPDT=8.

late group, asymmetric stretching of CH_3, asymmetric stretching of CH_2, symmetric stretching of CH_3, C=O stretching conjugated with the C=C groups of the acrylate and methacrylate groups, C=C stretching of a methacrylate group, C=C stretching of the acrylate group, respectively [19].

Figs. 5(b), (c) and (d) are the FTIR spectra of silica modified with AHM/TPDT=2, 4 and 8, respectively. The spectra have characteristic peaks of AHM at 3,108, 1,731 and 1,638 cm^{-1}, confirming the reaction of AHM with TPDT-modified silica. Comparing the FTIR spectrum of pure AHM in Fig. 5(a) with the spectra of AHM-modified silica in Fig. 5(b), (c) and (d), a disappearance of the $=CH_2$ peak of the acrylate group at 3,041 cm^{-1} and a shift of the C=O peak of pure AHM at 1,722 cm^{-1} was found for a higher wavenumber of 1,731 cm^{-1} for AHM-modified silica.

The disappearance of 3,041 cm^{-1} peak supports aza-Michael addition reaction between N-H groups of TPDT modified silica with acrylate groups of AHM. Also, The C=O peak shift to a higher wavenumber indicates that after the aza-Michael addition reaction of the acrylate group of AHM with the N-H group of TPDT, the acrylate group of AHM was saturated, in reducing the conjugation degree between the C=O group and the C=C group of AHM. For the quantitative analysis of the effects of the charged molar ratio of AHM/TPDT used to modify TPDT-modified silica, AR value changes calculated by Eq. (1) were investigated for the C=O peak of the acrylate and methacrylate groups at 1,731 cm^{-1} and the primary and secondary N-H stretching peaks at 3,297 cm^{-1}.

An increase in AR values was found for the peak at 1,731 cm^{-1} from 5.02, 7.15 and 10.99, but AR values for the peak at 3,297 cm^{-1} decreased from 0.53, 0.46 and 0.19 with the increase in the charged molar ratios of AHM/TPDT=2, 4 and 8.

With a gradual increase in the added molar ratios of AHM/TPDT from 2, 4 to 8, the reaction extent increased between the primary and secondary amino groups of TPDT grafted on the silica particles and acrylate groups of AHM; therefore, the increase of AR values for the C=O peak at 1,731 cm^{-1} originated from more AHM incorporation with the TPDT-modified silica particles. Correspondingly, the decrease of AR values for the N-H group at 3,297 cm^{-1} was due to the removal of the N-H groups by the aza-Michael addition reaction.

To investigate the reaction extent between the acrylate groups of AHM and the primary and secondary amino groups of TPDT grafted on the silica surface, EA analyses were performed and the results are shown in Table 3.

From the EA results, a decrease in the nitrogen content (%) from 1.94, 1.83 to 1.77 was observed. An increase in the carbon content also appeared from 8.91, 11.30 to 13.19 as the AHM/TPDT molar ratios were increased from 2, 4 to 8, due to the increase in the aza-Michael addition reaction of AHM to N-H groups in the TPDT-modified silica. These results are in accord with the FTIR results.

Table 3. Nitrogen and carbon contents with different AHM/TPDT mol ratios

AHM/ TPDT	Nitrogen [%]	Carbon [%]	Carbon [%]/ Nitrogen [%]
2	1.94	8.91	4.59
4	1.83	11.30	6.17
8	1.77	13.19	7.45

From the EA analysis results in Table 3, the theoretical C/N content ratios for the aza-Michael addition reaction between the primary and secondary amino groups of TPDT-grafted silica with the acrylate groups of AHM were calculated. The ratio was 4.86 if one N-H group of a total of four N-H groups of TPDT reacted with the acrylate groups of AHM; the ratio was 7.71 when two N-H groups reacted; the ratio was 10.57 when three N-H groups reacted; and finally, the ratio was 13.43 when all four N-H groups of TPDT reacted.

C/N content ratios were compared relative to the reaction conditions, and the highest C/N ratio found was 7.45 when AHM reacted with the N-H groups on the TPDT-modified silica at 50 °C for 3 h reaction time with AHM/TPDT molar ratio of 8. This result indicates that approximately 48% of the N-H groups on the TPDT-modified silica surface reacted with the acrylate groups of AHM; the remaining 52% of the groups did not undergo aza-Michael addition reaction.

Furthermore, this result supports the lower reactivity of the N-H groups on the TPDT-modified silica surface for the aza-Michael addition reaction due to the reduced mobility of the N-H groups attached on the solid silica surface and the steric hindrance by the solid silica particles.

The reaction between the N-H groups of TPDT grafted on the silica surface and the acrylate groups of AHM is a solid-liquid heterogeneous reaction; therefore, only a portion of the N-H groups on the silica surface can react with the acrylate group of AHM by the aza-Michael addition reaction [8].

5. Effect of Reaction Time and Temperature for the AHM Reaction

To study the effect of reaction time for the introduction of methacrylate groups when AHM reacted with TPDT-modified silica, a fixed reaction temperature of 50 °C was used while the reaction time was varied from 10 min, 30 min, 1 h, 2 h, 3 h to 5 h.

To quantitatively analyze the degree of the aza-Michael addition reaction depending on the reaction time, AR values for the C=O stretching peaks of the acrylate and methacrylate groups at 1,731 cm^{-1} and at the CH_2 bending peak at 1,464 cm^{-1} were calculated, respectively, using Eq. (1).

For the 1,731 cm^{-1} peak, an AR value increase was found to be 2.42, 4.54, 4.76, 5.61, 7.20 and 7.45, and the AR values for the 1,465 cm^{-1} peak were determined to be 0.84, 1.41, 1.51, 1.76, 1.83 and 1.91 with the increase in treatment time from 10 min, 30 min, 1 h, 2 h, 3 to 5 h, respectively.

By increasing the reaction time, the amount of reacted AHM to TPDT moiety increased on the silica surface due to the increased degree of the aza-Michael addition reaction between the acrylate group of AHM and the N-H group of TPDT.

Compared with the calculated AR values listed above, it is evident that a fast reaction rate occurred until 30 min and a slow reaction occurred from 30 min to 5 h, but most of the reaction was completed within 3 h reaction time.

To investigate the effects of reaction temperature, FTIR spectra

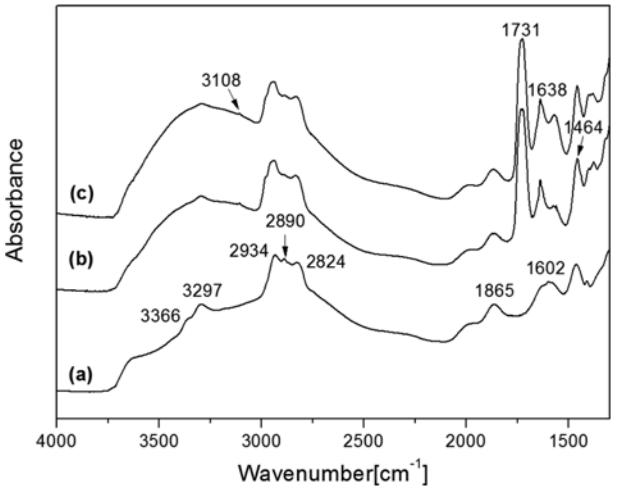

Fig. 6. FTIR spectra of (a) modified silica with TPDT/Si-OH=2; (b) modified silica with AHM/TPDT=4 at 25 °C; (c) modified silica with AHM/TPDT=4 at 50 °C.

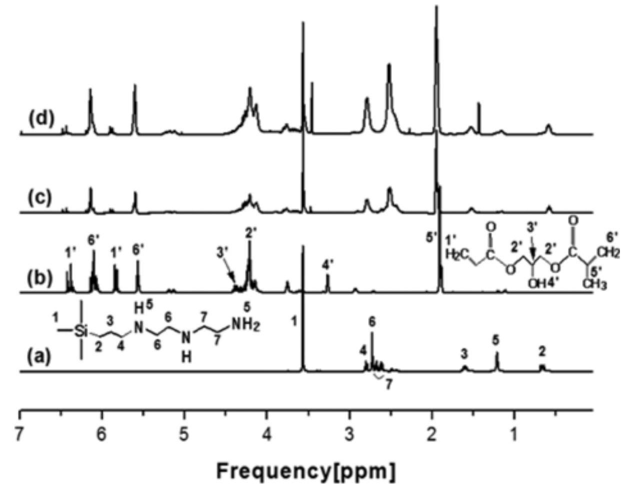

Fig. 7. ^{1}H NMR spectra of (a) neat TPDT; (b) neat AHM; (c) reacted at 25 °C; (d) reacted at 50 °C.

for AHM/TPDT=4 molar ratio reacted with TPDT/Si-OH=2 modified silica with at 25 and 50 °C for a fixed reaction time of 3 h were investigated, and the results are shown in Fig. 6.

Fig. 6(a) represents the FTIR spectrum of modified silica using only TPDT to modify the silica with a molar ratio of TPDT/Si-OH=2, and Fig. 6(b) and (c) are the FTIR spectra of modified silica with a molar ratio of AHM/TPDT=4 at 25 and 50 °C for TPDT/Si-OH=2 modified silica, respectively.

The AR values calculated for the 1,731 cm^{-1} peak from Eq. (1) are 7.05 and 7.38 for the 25 and 50 °C reaction temperatures, respectively. Comparatively, the AR values for the 1,464 cm^{-1} peak were calculated as 1.11 and 1.83 for the 25 and 50 °C reaction temperatures, respectively, supporting a higher degree of aza-Michael reaction between the N-H group of the TPDP moiety on the silica and the acrylate group of AHM for a 50 °C reaction temperature than for 25 °C.

The EA results also support the increase in the introduced amount of methacrylate groups on the TPDT-modified silica for the AHM modification reaction with a reaction temperature increase from 25 to 50 °C. The nitrogen content was reduced from 2.24 to 2.11%, but the carbon content increased from 4.74 to 4.87%. Therefore, the C/N ratios increased from 2.11 to 2.30. These results also exhibited the same trend as the FTIR results.

6. Liquid State ^{1}H and ^{13}C NMR Results

To quantitatively analyze the change in the N-H group structure after the aza-Michael addition reaction between the primary and secondary amino groups of the liquid state pure TPDT and the acrylate group of the liquid state pure AHM depending on the reaction temperature, the reaction time was fixed at 3 h for this study. The NMR spectra of the above reacted products were measured by changing the reaction temperature to 25 and 50 °C, and the results are shown in Fig. 7.

The ^{1}H NMR spectrum of neat TPDT in Fig. 7(a) shows peaks at 3.6, 2.8, 2.7, 2.6, 1.6, 1.2 and 0.7 ppm. The peak at 3.6 ppm was assigned as Si-OC$\underline{H}_3$, at 2.8 ppm as Si-CH$_2$CH$_2$C$\underline{H}_2$-NH, at 2.7 ppm as -NH-C$\underline{H}_2$C$\underline{H}_2$-NH-, at 2.6 ppm as -NH-C$\underline{H}_2$C$\underline{H}_2$-NH$_2$, at 1.6 ppm as Si-CH$_2$C$\underline{H}_2$, at 1.2 ppm as primary and secondary N-$\underline{H}$, and at 0.7 ppm as Si-C$\underline{H}_2$.

The ^{1}H NMR spectrum of neat AHM in Fig. 7(b) shows peaks at 6.4, 6.1, 5.9, 5.6, 4.4, 4.2, 3.3 and 1.9 ppm. The peaks at 6.4 and 5.9 ppm were assigned as C$\underline{H}_2$=C$\underline{H}$ of the acrylate group, at 6.1 and 5.6 ppm as C$\underline{H}_2$=C of the methacrylate group, at 4.4 ppm as C$\underline{H}$-OH, at 4.2 ppm as two -OC$\underline{H}_2$, at 3.3 ppm as -O$\underline{H}$, and at 1.9 ppm as -C$\underline{H}_3$ [20].

Figs. 7(c) and (d) are the ^{1}H NMR spectra of the 3 h reaction products between neat TPDT and neat AHM at 25 and 50 °C, respectively. The area ratios of the N-H peak at 1.2 ppm to the reference peak of Si-CH$_2$ at 0.7 ppm decreased from 1.73 for neat TPDT to 0.42 (76% reaction) and 0.29 (83% reaction) for the reaction products at 25 and 50 °C, respectively. These results also support the occurrence of more aza-Michael reaction with increased reaction temperature from 25 to 50 °C, and the degree of the aza-Michael reaction over 75% for the above two reactions indicates secondary amino groups produced by reaction of primary amino groups of TPDT with acrylate groups of AHM partially react with acrylate groups of AHM.

The ^{1}H NMR analysis results indicated that 83% of the N-H groups of TPDT reacted with the acrylate groups of AHM through the aza-Michael addition reaction between neat TPDT and neat AHM at 50 °C. However, approximately 48% of the N-H groups of the TPDT-modified silica reacted with the acrylate groups of AHM based on the above EA results, which is lower than that between neat TPDT and neat AHM.

It is postulated that the lower degree of aza-Michael addition reaction between TPDT-modified silica and AHM than between neat TPDT and neat AHM is caused by the reduced mobility of the N-H groups of TPDT attached on the silica particles and the steric hindrance effect by the solid silica particles [8].

The effect of 10-min, 1 h, 2 h and 5 h reaction times on the reactivity of the primary and secondary N-H groups of TPDT was also studied for the reaction between neat TPDT and neat AHM at 50 °C by measuring the liquid state ^{13}C NMR spectra, as shown in Fig. 8.

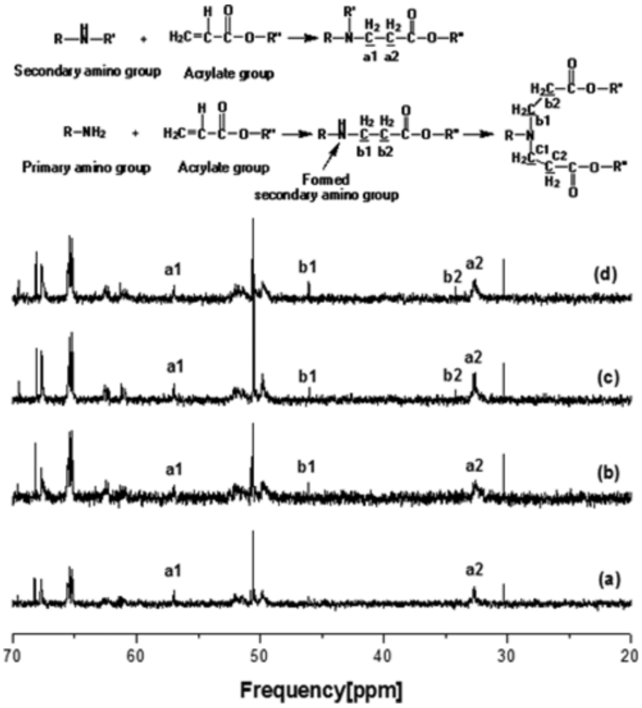

Fig. 8. ^{13}C NMR spectra of reaction products between neat TPDT and neat AHM: (a) for 10 min; (b) for 1 h; (c) for 2 h; (d) for 5 h.

From the result, a1 and a2 peaks at 56.8 and 32.9 ppm for the 10 min reaction time were found, due to the reaction products of the secondary amino group of TPDT with the acrylate group of AHM. When the reaction time was increased from 10 min to 1 h, 2 h and 5 h, however, additional peaks of b1 and b2 appeared at 46.1 and 34.2 ppm, respectively, which are caused by the products of the reaction between the primary amino groups of TPDT with the acrylate groups of AHM.

As a result, a preferential reaction of the secondary amino group of TPDT with the acrylate group of AHM was found through the aza-Michael addition reaction. After 10 min of reaction, however, the primary amino groups that were known to have lower reactivity than the secondary amino groups started to react with the acrylate group of AHM [21].

If 83% of total N-H groups of pure TPDT react with acrylate groups of AHM, a fraction of secondary amino groups formed after aza-Michael reaction between primary amino groups of TPDT with acrylate groups of AHM must react; the appearance of two c1 and c2 peaks at 56.4 and 33.6 ppm positions, respectively, were expected.

However, c1 and c2 peaks appeared adjacent to a1 and a2 peaks, and only a fraction of the secondary amino groups formed after the aza-Michael addition reaction of primary amino groups of TPDT with acrylate groups of AHM will react due to high steric hindrance of generated secondary amino groups by the AHM bonded with the primary amino groups of TPDT [22]. Therefore, it was difficult to find c1 and c2 peaks clearly from Fig. 8.

7. Solid state ^{29}Si NMR Results

The ^{29}Si NMR spectra of pristine silica and TPDT-modified silica were measured to study the structure of the reaction products, as shown in Fig. 9.

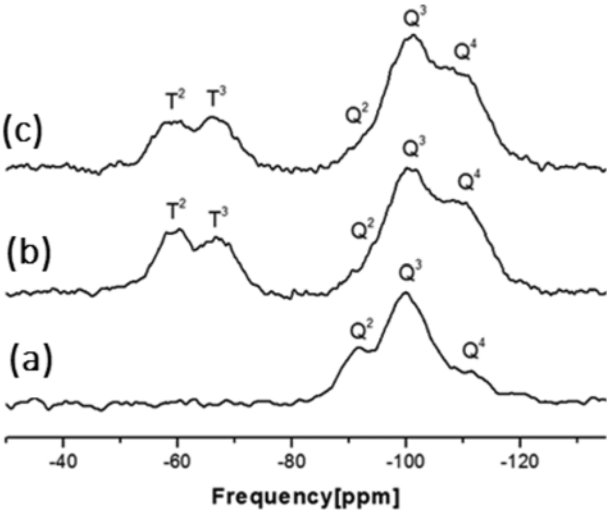

Fig. 9. ^{29}Si NMR spectra of (a) pristine silica; (b) modified silica with TPDT/Si-OH=1; (c) modified silica with TPDT/Si-OH=2.

The NMR spectrum of pristine silica shown in Fig. 9(a) shows peaks at −90.6, −99.7 and −110.6 ppm, due to $Q^2(SiO_2(OH)_2)$, $Q^3(SiO_3OH)$ and $Q^4(SiO_4)$, respectively. However, the NMR spectra for modified silica with TPDT at molar ratios of TPDT/Si-OH=1 and TPDT/Si-OH=2 shown in Fig. 9(b) and (c), respectively, have new additional peaks at −60.2 and −66.8 ppm due to the $T^2(SiO_2OHR')$ and $T^3(SiO_3R')$ of the newly introduced Si of TPDT, supporting the introduction of TPDT onto the silica surface [23].

To quantitatively compare changes in the peaks of the ^{29}Si NMR spectra illustrated in Fig. 9, the area change in peaks by curve-fitting using the PeakFit^{TM} V4.00 (AISN Software, Inc.) program was calculated. From the result, a decrease in the Q^2 area % for pristine silica from 27.8% to 14.9 and 12.8% and the Q^3 area % from 53.1% to 47.4 and 46.3% was observed when the TPDT/Si-OH molar ratios were increased from 1 to 2. Conversely, the area % of Q^4 for pristine silica increased from 19.1% to 37.7 and 40.9% after TPDT silanization with silica.

In addition, a decrease in the T^2 peak area % from 52.0 to 48.8% and an increase in the T^3 peak from 48.0 to 51.2% were found from the analysis. These results support the higher amount of T^3 structural formation than T^2 structural formation by the increase of the TPDT/Si-OH molar ratio from 1 to 2.

CONCLUSIONS

Experiments were conducted by various analysis techniques to elucidate the effect of introducing free radical polymerizable methacrylate groups on a silica particle surface by the aza-Michael addition reaction between acrylate groups of AHM and N-H groups of TPDT-modified silica.

Most of the silanization reaction between the Si-OH groups on the silica particle surface and TPDT occurred within 2 h reaction time when using pre-hydrolyzed TPDT. In addition, an increase in the grafted TPDT amount on the silica surface was observed by increasing the input molar ratio of TPDT/Si-OH.

For the aza-Michael addition reaction between acrylate groups of AHM with the amino groups of the TPDT moiety on the TPDT-modified silica surface, increasing the molar ratio of AHM/TPDP and reaction temperature played an important role in increasing the degree of aza-Michael reaction. For instance, according to the liquid ^{1}H NMR spectra, we concluded that approximately 76% of the N-H groups of TPDT reacted at 25 °C compared with approximately 83% at 50 °C. These results suggest that degree of reaction was strongly dependent on the reaction temperature. In addition, preferential aza-Michael addition reaction between the secondary amino groups of TPDT with the acrylate groups of AHM was observed from the liquid state ^{13}C NMR spectrum results.

Finally, when comparing the two aza-Michael addition reactions of pure AHM with pure TPDT and pure AHM with TPDT-modified silica particles, approximately 83% of the total N-H groups of pure TPDT reacted with the acrylate groups of AHM, but approximately 48% of the total N-H groups of TPDT-modified silica particles reacted with the acrylate groups of pure AHM at the same reaction condition. These results are likely due to the lower mobility of the amino groups of the TPDT moiety grafted on the solid silica particles and the higher steric hindrance by the solid silica particles since the heterogeneous reaction has a higher steric hindrance than that of homogeneous reaction between AHM and TPDT.

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