

# Thermal and Mechanical Properties of Photocured Organic–Inorganic Hybrid Nanocomposites of Terpene-Based Acrylate Resin and Methacrylate-Substituted Polysilsesquioxane

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**ABSTRACT:** Diacrylate compounds derived from  $\alpha$ -pinene and limonene (TDAs: TDA-1 and TDA-2) were photocured with methacryl-substituted polysilsesquioxane (ME-PSQ) prepared from 3-(trimethoxysilyl)propyl methacrylate and tetramethylammonium hydroxide (TMAOH) in the TDA/ME-PSQ weight ratio of 20 : 0, 20 : 1, 20 : 2, 20 : 3, and 20 : 4. All the photocured TDA/ME-PSQ hybrid nanocomposites became transparent. The thermo-mechanical analysis of the cured TDA/ME-PSQ revealed that the glass transition temperature ( $T_g$ ) increased, the thermal expansion coefficient above  $T_g$  decreased with increasing ME-PSQ content, and that the TDA-1/ME-PSQ had ca. 30°C greater  $T_g$  than the TDA-2/ME-PSQ with the same ME-PSQ content. Also, the dynamic mechanical anal-

ysis revealed that the TDA-1/ME-PSQ had much greater storage modulus at around 150°C than the corresponding TDA-2/ME-PSQ. The flexural strength and modulus of the TDA/ME-PSQ nanocomposites at 20°C had maximum at ME-PSQ content 4.8 and 13.0 wt %, respectively. As a whole, the thermal and mechanical properties of the nanocomposites were improved by the addition of ME-PSQ, and those of TDA-1/ME-PSQ nanocomposites were superior to those of TDA-2/ME-PSQ. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 3326–3331, 2010

**Key words:** nanocomposites; renewable resources; photopolymerization; terpene; silsesquioxane

## INTRODUCTION

Bio-based polymers and composites derived from annually renewable agricultural and biomass feedstock have become increasingly important as sustainable and eco-efficient products that can replace the products based on petroleum feedstock.<sup>1,2</sup> Among the renewable natural resources, monoterpenes such as D-limonene and pinenes are cheap and abundant unsaturated cyclic hydrocarbons obtained from the rind of citrus fruit and pine trees, respectively. D-Limonene has been used as flavoring in food manufacturing, botanical insecticides, industrial and household cleaning products, and solvents.<sup>3,4</sup>  $\alpha$ - and  $\beta$ -pinenes have been used as industrial solvents and raw materials for fragrant chemical compounds.<sup>3,5</sup> In addition, polymerization products<sup>6–8</sup> and phenol resins<sup>9–11</sup> derived from limonene and pinene have been used as tackifiers and epoxy harders. However, these terpene-based polymeric materials have generally poor heat resistance and mechanical strength and have not been widely used in various applications.

Organic–inorganic hybrid nanocomposites by the reaction of polysilsesquioxanes ( $(RSiO_{3/2})_n$ ) with organic functional groups with organic monomers, oligomers, and polymers possessing functional groups are expected to have increased performance capabilities relative to the former nonhybrid nanocomposites.<sup>12–19</sup> We had already reported the thermal and mechanical properties of the organic–inorganic hybrid nanocomposites of itaconate unit-incorporated poly(butylene succinate)<sup>20</sup> and vinyl ester resin<sup>21</sup> with methacryl group-substituted polysilsesquioxanes (ME-PSQ) prepared from 3-(trimethoxysilyl)propyl methacrylate (TMSPM).

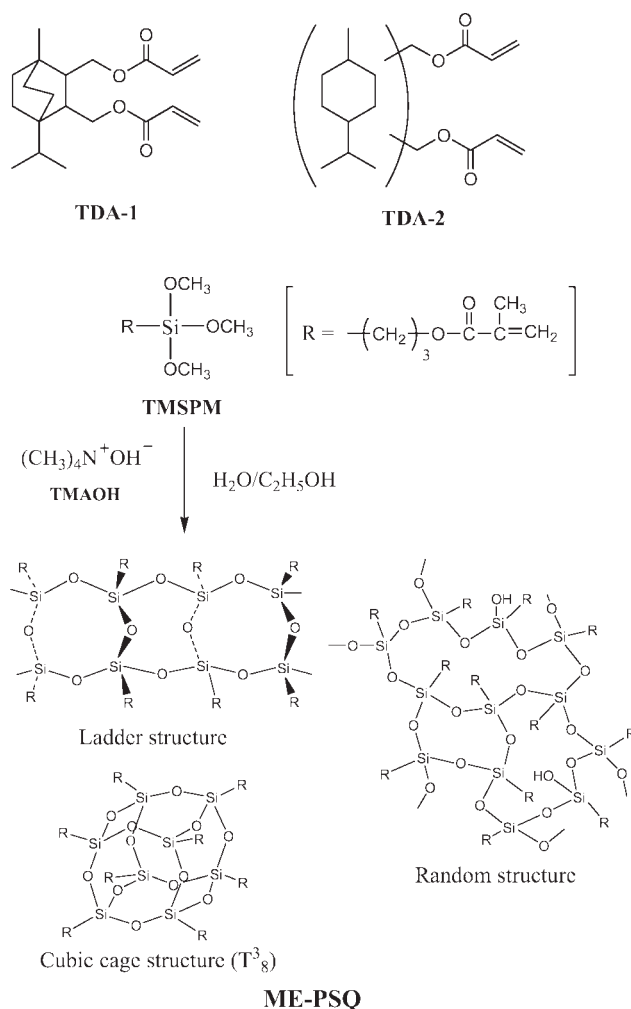
In this study, to improve the thermal and mechanical properties of diacrylate compounds (TDAs: TDA-1 and TDA-2) derived from  $\alpha$ -pinene and limonene, the TDA-1 and TDA-2 were photocured with ME-PSQ to give terpene-based organic–inorganic hybrid nanocomposites.

## EXPERIMENTAL

### Materials

Diacrylate compounds derived from  $\alpha$ -pinene and limonene (TDAs: TDA-1 and TDA-2) were kindly supplied from Yasuhara Chemical (Fuchu, Hiroshima,

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**Figure 1** Structures of TDA-1 and TDA-2 and synthetic scheme of ME-PSQ.

Japan). The structures of TDA-1 and TDA-2 are shown in Figure 1. Photoinitiators, 1-hydroxycyclohexyl phenyl ketone (Irgacure 184, mp. 45–49°C, UV/VIS absorption peaks in methanol: 246, 280, 333 nm) and phenyl bis(2,4,6-trimethylbenzoyl)phosphine oxide (Irgacure 819, mp. 127–133°C UV/VIS absorption peaks in methanol: 295, 370 nm) were kindly supplied from Chiba Specialty Chemicals K.K. (Tokyo, Japan). 3-(Trimethoxysilyl)propyl methacrylate and 10 wt % tetramethylammonium hydroxide in water were purchased from Sigma-Aldrich Japan (Tokyo, Japan).

### Preparation of ME-PSQ

The synthetic scheme of ME-PSQ is shown in Figure 1. 3-(Trimethoxysilyl)propyl methacrylate (20 mL, 84 mmol) was added to a mixture of ion-exchanged water (25 mL), ethanol (75 mL), and 10 wt % tetramethylammonium hydroxide aqueous solution (1.0 mL, 1.1 mmol). The mixture was stirred for 24 h at

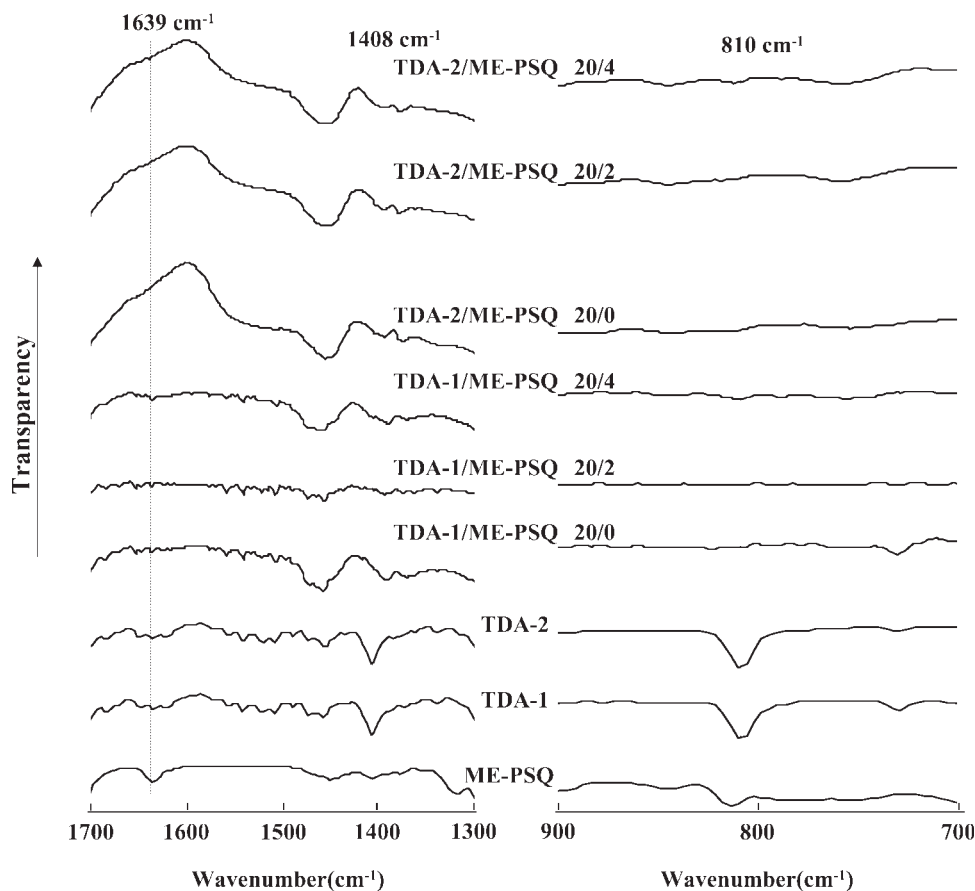
room temperature and allowed to stand for 1 day. The formed precipitate was collected by decantation, washed by vacuum filtration with ion-exchanged water/ethanol (1/3 by volume), and then washed again with ethanol. The rinsed product was dried under vacuum for 24 h at room temperature to give ME-PSQ (8.4 g) as a colorless viscose liquid in 56% yield. The  $M_n$  and  $M_w$  measured by GPC using polystyrene standards for ME-PSQ were 5900 and 15,000, respectively. Because the theoretical molecular weight of the corresponding fully condensed  $\text{T}_8^3$  cubic polyhedral oligomeric silsesquioxane (POSS) derivative is 1432, the content of ladder and random polysilsesquioxanes and/or bigger POSS ( $\text{T}_{10}^3$ ,  $\text{T}_{12}^3$ , and  $\text{T}_{14}^3$ , etc.) for ME-PSQ is relatively larger than cubic  $\text{T}_8^3$  POSS, as is shown in Figure 1.<sup>20,21</sup>

### Preparation of TDA/ME-PSQ hybrid nanocomposites

A solution of ME-PSQ (0.30 g, methacryl group 1.67 mmol) in acetone (2.0 mL), irgacure 184 (23 mg, 0.11 mmol), and irgacure 819 (4.6 mg, 0.011 mmol) as surface and through cure initiators, respectively, were added to TDA-1 (2.00 g, 5.94 mmol) in a  $\phi$  45 mm poly(tetrafluoroethylene) culture dish. The mixture was stirred for 2 h at room temperature and then vacuum dried at 55°C for 2 h. The obtained homogenous transparent mixture was photocured at room temperature for 30 s to give a TDA-1/ME-PSQ 20/3 nanocomposite film (thickness: ca. 1.2 mm) with ME-PSQ content 13.0 wt %. SPOT-CURE SP-7 (250 W light source, wavelength 240–440 nm, Ushio, Yokohama, Japan) was used for the photocuring (irradiation intensity 97 mW/cm<sup>2</sup>). The TDA-1/ME-PSQ nanocomposites with the weight ratio 20/0, 20/1, 20/2, and 20/4 were prepared in a similar manner to the TDA-1/ME-PSQ 20/3 composite. Also, TDA-2/ME-PSQ composites with the weight ratio 20/0, 20/1, 20/2, 20/3, and 20/4 were prepared in a similar manner to the TDA-1/ME-PSQ nanocomposites.

### Measurements

Fourier transform infrared (FTIR) spectra were recorded on a FTIR 8100 (Shimadzu, Kyoto, Japan) by the KBr-pellet or attenuated total reflectance method. Thermomechanical analysis (TMA) was conducted on a TMA 4000S (MAC Science, Yokohama, Japan) at a heating rate of 10°C/min at a nitrogen atmosphere. Dynamic mechanical analysis (DMA) of the rectangular plates (length 30 mm, width 8 mm, thickness 1.2 mm) was performed on a Rheograph Solid (Toyo Seiki, Tokyo, Japan) with a chuck distance of 20 mm, a frequency of 10 Hz, and a heating rate of 2°C/min. The 5% weight loss temperature was measured on a Shimadzu TGA-50



**Figure 2** FTIR spectra of TDA-1, TDA-2, ME-PSQ, and the hybrid composites.

thermogravimetric analyzer at a heating rate of 20°C/min in a nitrogen atmosphere. Flexural test of the rectangular plates (length 30 mm, width 8 mm, thickness 1.2 mm) was performed with use of a Shimadzu Autograph AGS-500C based on the standard method for testing the flexural properties of plastics (JIS K7171-2008, ISO 178-2001). Span length was 20 mm, and the testing speed was 10 mm/min. Five composite specimens were tested for each set of samples, and the mean values and the standard deviation were calculated.

## RESULTS AND DISCUSSION

### Characterization of TDA/ME-PSQ hybrid nanocomposites

Figure 2 shows the FTIR spectra of the photocured TDA-1/ME-PSQ and TDA-2/ME-PSQ hybrid nanocomposites. In the IR spectra of TDA-1, TDA-2, and ME-PSQ, the absorption peak at 1639  $\text{cm}^{-1}$  is assigned to the stretching of vinyl attached to carbonyl group and the peaks at 1408 and 810  $\text{cm}^{-1}$  are corresponding to olefinic C—H group in-plane and out-of-plane bending. Their absorption peaks related to the vinyl group disappeared in the FTIR spectra

of the photocured TDA/ME-PSQ 20/0 and 20/2 samples. However, their absorption peaks were slightly remaining for the nanocomposites with the TDA/ME-PSQ ratio 20/4, suggesting that slight amount of the methacryl groups connected to rigid polysilsesquioxane framework in ME-PSQ are remaining as the result of steric hindrance.

All the photocured TDA/ME-PSQ nanocomposites became homogeneous and transparent films. The average percent transmittance ( $T\%$ ) of visible light between 380 and 780 nm for the film samples with the thickness of *ca.* 1.2 mm are summarized in Table I. All the TDA-1/ME-PSQ composites showed almost the same transmittance as photocured TDA-1, suggesting the nanocomposites sustain a good transparency. The  $T\%$  of the TDA-2/ME-PSQ nanocomposites was a little lower than that of photocured TDA-2, indicating the occurrence of a slight aggregation of the silsesquioxane component.

### Thermal properties of TDA/ME-PSQ hybrid nanocomposites

Table I summarizes glass transition temperature ( $T_g$ ) and coefficient of thermal expansion measured by

TABLE I  
Transmittance of Visible Light and TMA Data for TDA/ME-PSQ Hybrid Composites

Photocured sample	Weight ratio of TDA/ME-PSQ	ME-PSQ content (wt %)	$T$ %	$T_g$ ( $^{\circ}\text{C}$ )	$\alpha_1$ ( $1/^{\circ}\text{C}$ )	$\alpha_2$ ( $1/^{\circ}\text{C}$ )
TDA-1/ME-PSQ	20/0	0	68.1	151.4	84	250
	20/1	4.8	69.9	157.0	76	140
	20/2	9.1	69.3	159.9	87	128
	20/3	13.0	68.7	166.9	82	111
	20/4	16.7	69.8	179.1	88	109
TDA-2/ME-PSQ	20/0	0	61.1	121.8	88	153
	20/1	4.8	59.0	134.9	87	149
	20/2	9.1	56.5	135.7	84	141
	20/3	13.0	57.0	140.1	86	127
	20/4	16.7	57.9	148.4	96	136

TMA for the TDA/ME-PSQ nanocomposites. For all the nanocomposites, the  $T_g$  increased with increasing ME-PSQ content. Also, coefficient of thermal expansion above  $T_g$  ( $\alpha_2$ ) decreased with increasing ME-PSQ content. The addition of multifunctional ME-PSQ causes the increase of crosslinking density and restriction of molecular motion by the interaction of the rigid polysilsesquioxane moiety, especially at increased temperatures. The TDA-1/ME-PSQ nanocomposites had greater  $T_g$  by ca.  $30^{\circ}\text{C}$  than the TDA-2/ME-PSQ nanocomposites with the same ME-PSQ content. This result should be attributed to the fact that TDA-1 has a more rigid [2.2.2]bicyclooctane framework than TDA-2 with cyclohexane framework and that two adjacent acrylate groups of TDA-1 are sterically hindered and their molecular motion are restricted.

Figure 3 shows the temperature dependence of storage modulus ( $E'$ ) measured by DMA for the TDA/ME-PSQ nanocomposites. As a whole, the  $E'$  over the temperature range from 0 to  $250^{\circ}\text{C}$  increased with increasing ME-PSQ content. The  $E'$  for TDA/ME-PSQ 20/4 nanocomposites was exceptionally lower than that for the 20/3 composite. The temperature at the maximum of loss modulus ( $E''$ ) measured by DMA, which is corresponding to  $T_g$ , is summarized in Table II. The  $T_g$  by DMA for the TDA/ME-PSQ nanocomposites increased with increasing ME-PSQ content until 13.0 wt %, in a similar manner to the result of the  $T_g$  by TMA. The TDA/ME-PSQ nanocomposites with ME-PSQ content 16.7 wt % showed slightly lower  $T_g$  than the corresponding nanocomposites at 13.0 wt %. The reason why the 20/4 nanocomposites showed a lower  $E'$  and  $T_g$  may be attributed to the fact that some methacryl group is remaining for the 20/4 nanocomposites. The TDA-1/ME-PSQ nanocomposites had  $32$ – $62^{\circ}\text{C}$  greater  $T_g$  (DMA) than the TDA-2/ME-PSQ nanocomposites with the same ME-PSQ content. Also, the  $E'$  at approximately  $150^{\circ}\text{C}$  for the former nanocomposites was much greater than the latter nanocomposites.

Table II summarizes 5% weight loss temperature measured by TGA for the hybrid nanocomposites. The thermal degradation temperature of the TDA/

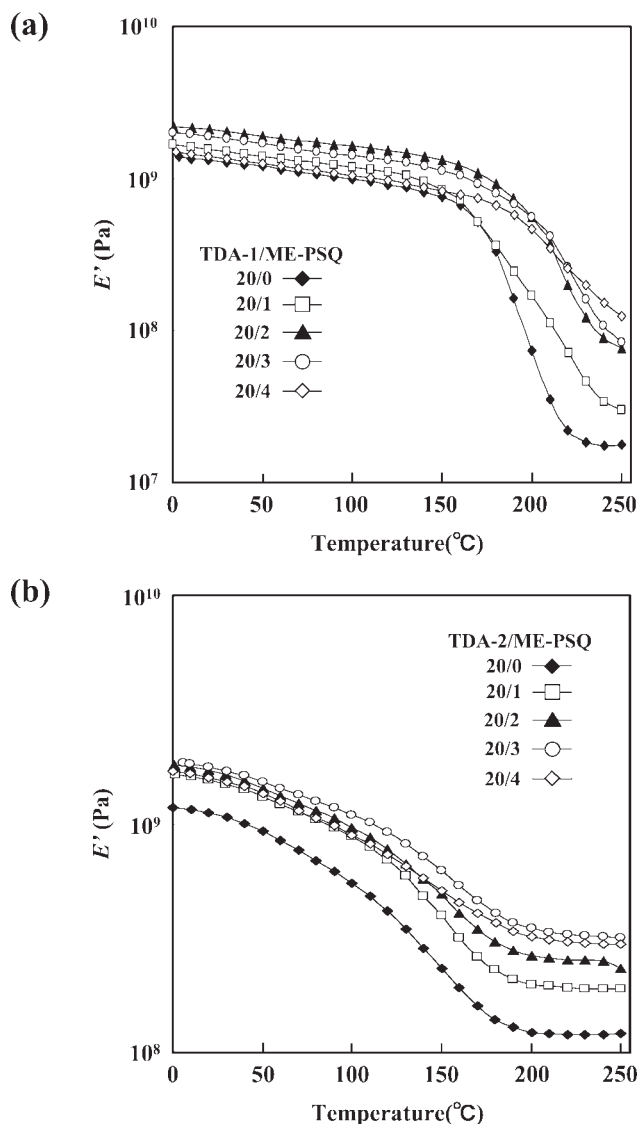


Figure 3 Temperature dependence of storage modulus measured by DMA for TDA-1/ME-PSQ and TDA-2/ME-PSQ hybrid composites.

**TABLE II**  
**Glass Transition Temperature Measured by DMA**  
**and 5% Weight Loss Temperature for TDA/ME-PSQ**  
**Hybrid Composites**

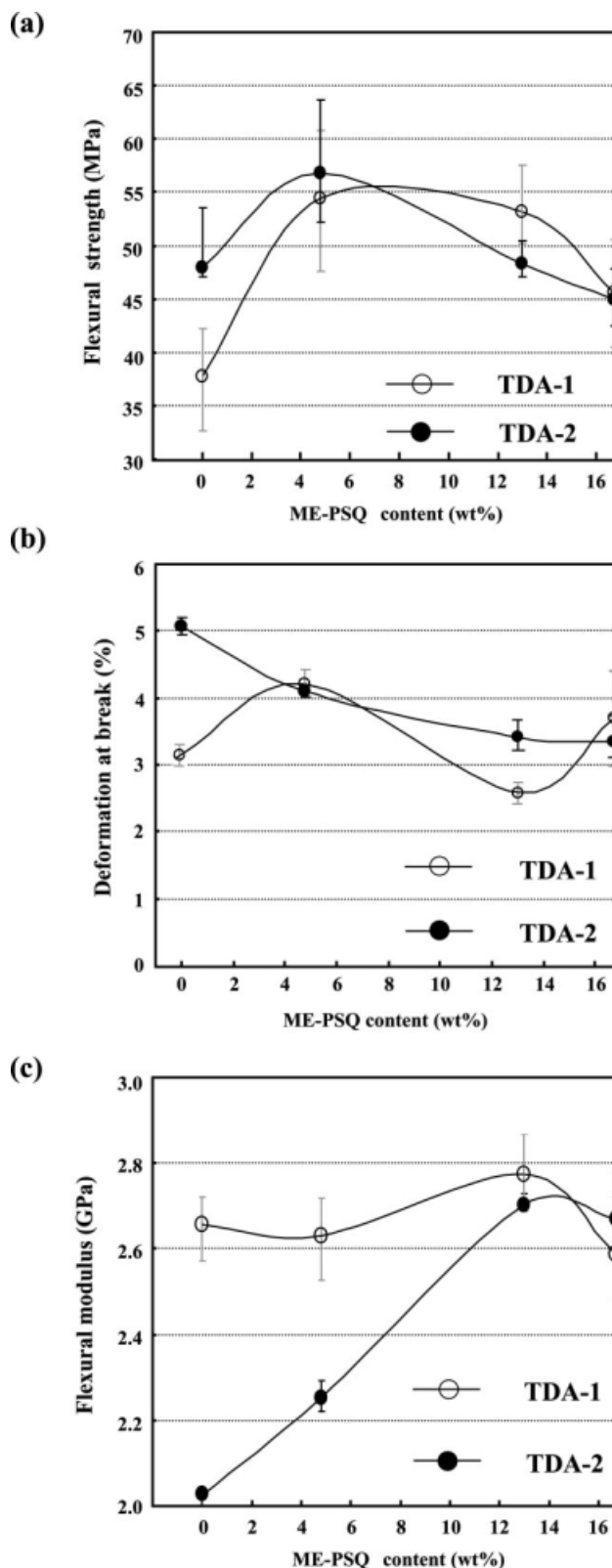
	ME-PSQ content (wt %)	$T_g$ (°C) [DMA]	5 wt % loss temp. (°C)
TDA-1/ME-PSQ	0	177.9	411
	4.8	172.8	414
	9.1	174.8	416
	13.0	208.9	417
	16.7	203.9	420
TDA-2/ME-PSQ	0	141.3	421
	4.8	140.9	419
	9.1	142.9	425
	13.0	146.5	425
	16.7	142.3	424

ME-PSQ hybrid nanocomposites was a little greater than that of the photocured TDA. The incorporation of ME-PSQ moiety had little influence on the thermal degradation temperature, although the char yield at around 500°C for the hybrid nanocomposites increased with increasing ME-PSQ content.

#### Flexural properties of TDA/ME-PSQ hybrid nanocomposites

Figure 4 shows the flexural properties of TDA-1/ME-PSQ and TDA-2/ME-PSQ nanocomposites. For both the nanocomposites, the flexural strength had a maximum value at ME-PSQ content 4.8 wt %, and a little decreased with a greater ME-PSQ content. The decrease is attributed to an increase of brittleness by the addition of ME-PSQ for the TDA-2/ME-PSQ nanocomposites, as is obvious from the decrease of deformation at break with ME-PSQ content. We could not elucidate a clear relation between the deformation at break and ME-PSQ content for the TDA-1/ME-PSQ nanocomposites, probably due to the fact that the photocured TDA-1 itself was more brittle and stiffer than the photocured TDA-2. There was little difference in tensile strength between TDA-1/ME-PSQ and TDA-2/ME-PSQ nanocomposites in the ME-PSQ content 4.8 to 16.7 wt % range, when the error bar was considered. The flexural modulus of TDA-1/ME-PSQ and TDA-2/ME-PSQ nanocomposites had a maximum at ME-PSQ content 13.0 wt %. The flexural modulus of the TDA-2 nanocomposites was much improved by the addition of ME-PSQ, while the modulus of the TDA-1 nanocomposites little increased. However, because the photocured TDA-1 had much higher flexural modulus than the photocured TDA-2, TDA-1/ME-PSQ showed a greater flexural modulus than TDA-2/ME-PSQ at ME-PSQ content 4.8 and 13.0 wt %. The fact that the TDA/ME-PSQ nanocomposites with ME-PSQ content 16.7 wt % showed a lower flexural

strength and modulus is attributed to incomplete photocuring reaction of the methacryl group of ME-PSQ, as is obvious from the result of FTIR.



**Figure 4** Flexural properties of TDA-1/ME-PSQ and TDA-2/ME-PSQ hybrid composites.

## CONCLUSIONS

Thermal and mechanical properties of the hybrid nanocomposites prepared by the photocuring reaction of TDA-1 or TDA-2 with ME-PSQ were investigated by means of TMA, DMA, TGA, and flexural test. All the photocured TDA/ME-PSQ hybrid nanocomposites became transparent homogenous materials. As a whole,  $T_g$  increased and thermal expansion coefficient above  $T_g$  for the cured TDA/ME-PSQ decreased with increasing ME-PSQ content. The TDA-1/ME-PSQ nanocomposites had higher  $T_g$  than the TDA-2/ME-PSQ nanocomposites with the same ME-PSQ content. The  $E'$  at approximately 150°C for the former nanocomposites was also much greater than the latter nanocomposites. The incorporation of ME-PSQ moiety into the terpene-based acrylate networks had little influence on the thermal degradation temperature. The flexural strength and modulus of the TDA/ME-PSQ nanocomposites at 20°C had maximum at ME-PSQ content 4.8 and 13.0 wt %, respectively. There was little difference in flexural strength between TDA-1/ME-PSQ and TDA-2/ME-PSQ nanocomposites. The flexural modulus of the TDA-2 nanocomposites was much improved by the addition of ME-PSQ, while the modulus of the TDA-1 nanocomposites little increased. However, because the cured TDA-1 had a much greater modulus than the cured TDA-2, TDA-1/ME-PSQ (20/1-20/3) nanocomposites showed rather greater flexural modulus than TDA-2/ME-PSQ (20/1-20/3) nanocomposite. As a result, TDA-1/ME-PSQ is a bio-based photocurable material with excellent heat resistance, mechanical properties, and transparency.

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