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LETTER

Controlling POSS dispersion in epoxy in nanocomposite by introducing multi-epoxy POSS groups

**Yen-Zen Wang · Huang-Shian Tsai ·
Zhao-Yu Ji · Wen-Yi Chen**

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Introduction

In recent years, polyhedral oligomeric silsesquioxanes derivatives, providing nano-reinforcement, have been extensively employed to reinforce polymers by forming a nanocomposite. Incorporating POSS particles into linear thermoplastics or thermosetting networks markedly improves the thermal [1], dimensional stability [1] and oxidative [2] properties of several polymer resins, extending their applications as high-performance engineering plastics. Numerous thermoplastics and some thermosetting systems have thus been enhanced. These include methacrylates, [3, 4] styrenes, [5] norbornenes, [6] siloxanes [7] and epoxies [1, 8–11]. Multi-functional POSS derivatives such as epoxy resin, [1, 8–11] polyurethane, [12] polyacrylate, [13] polyimide, [14, 15] and polybenzoxazine [16, 17] have been utilized as curing junctions, further increasing the crosslinking density of the polymer. Introducing ''multi-functional'' POSS derivatives results in interesting thermal and mechanical characteristics. Two of the factors that significantly affect the thermal and mechanical characteristics of the nanocomposite systems are the crosslinking density and the dispersion state of nanofillers in the nanocomposite matrix. According to the character of substituents, types of the aggregated POSS within matrix could behave either as nanofiller reinforcing the matrix or as the plasticizer. In particular, the dispersion of nanofillers in the nanocomposite matrix is an important issue that has been studied by many scientists, because the crosslinking density [18] of the nanocomposite is related to the dispersion of the nanofillers therein. In nanocomposites with multi-functional POSS derivatives, POSS derivatives can react with the monomer units of the polymer, increasing their crosslinking density [12, 16, 19]. In some cases [15, 20–23], the POSS derivatives react with the monomers of the polymer. The POSS that is aggregated inside the nanocomposite matrix behaves as the plasticizer, as revealed by the less favorable thermal properties.

In this work, dynamic curing kinetics were utilized to evaluate the reactivity between the soft epoxy/DDM system and cured derivatives of multi-functional POSS (OG) (The octaepoxy-POSS monomer (OG) has eight epoxide functional groups). The reactivity between soft epoxy and OG cured with a DDM, enables further the dispersion state of POSS in the nanocomposite matrix to be verified. Based on the assumption that OG reacts with DDM more rapidly than does soft epoxy that has been cured with DDM, since DDM is inserted into OG such that the aggregation declines as OG reacts with DDM, the reactivity of nanocomposite by multi-functional derivatives octaepoxy-POSS will be investigated by introducing multi-functional POSS derivates to understand the POSS dispersion state of nanocomposite.

Experimental

Materials

The diglycidylether of 2,2′-propandiol (soft epoxy, its chemical structure is shown in Fig. 1) was purchased from Chang-Chun Chemical Company, Taiwan. The diglycidyl ether of bisphenol-A (DER 331, EEW = 190 g/equiv.)

Y.-Z. Wang (✉) · Z.-Y. Ji · W.-Y. Chen
Department of Chemical Engineering, National Yunlin
University of Science and Technology, Yun-Lin 640, Taiwan
e-mail: wangzen@yuntech.edu.tw

Y.-Z. Wang · H.-S. Tsai
Graduate School of Engineering Science and Technology
(Doctoral Program), National Yunlin University of Science &
Technology, Yunlin 640, Taiwan

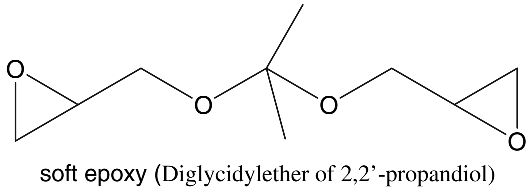


Fig. 1 Chemical structure of soft epoxy (Diglycidylether of 2,2′-propandiol)

was purchased from Dow Chemical Company, USA. The OG was purchased from Hybrid Plastics Chemical Company, USA. Meta-phenylenediamine (mPDA) and 4,4′-diaminodiphenylmethane (DDM) were purchased from Acros, Belgium.

Dynamic curing kinetics

The dynamic curing kinetics of OG/DDM and soft epoxy/DDM were studied using a Du-Pont Q100 Differential Scanning Calorimeter in an atmosphere of nitrogen. The sample (approximately 7 mg) was placed in a sealed aluminum sample pan. A dynamic curing scan was performed from 30 to 350 °C at a heating rate of 10, 20, 30 or 40 °C/min.

Preparation of cured samples

Stoichiometric amounts of soft epoxy/DDM that contained various amounts OG were mixed with acetone in a high-speed stirrer, with stirring for 10 min. After it had been degassed under vacuum and the solvent had been removed, the soft epoxy/DDM/OG was clear and homogeneous, but the other system DGEBA/mPDA/OG, was heterogeneous. The mixture was cured at 120 °C for 120 min before thermal and heat-resistance properties were evaluated. The same conditions were applied to prepare the DGEBA/mPDA/OG system.

Characterizations

Each sample was placed on a KBr pellet and FTIR spectra were obtained at a constant temperature of 120 °C using a Nicolet AVATAR 320 FT-IR spectrometer (Madison, Wisconsin, USA) at a resolution of 2 to measure the rate of epoxide conversion in the system. Scanning electron microscopy (SEM) was performed using an environmental scanning electron microscope (ESEM).

Results and discussion

Reactivity of curing agent, epoxy and epoxy-POSS

Kinetic analysis was performed using two kinetic models—the Kissinger and the Flynn–Wall–Ozawa models [24–26]. Based on the Kissinger method, the activation energy is obtained from the maximum reaction rate where *d(da/dt)/dt* is zero at a constant-heating-rate. The derived relationship is given by

$$\frac{d\left[\ln\left(q/T_p^2\right)\right]}{d\left(1/T_p\right)} = -\frac{E_a}{R} \tag{1}$$

where T_p is the temperature at which the rate is maximized and q is the constant heating rate. Accordingly, a plot of $\ln\left(q/T_p^2\right)$ versus $1/T_p$ yields the activation energy, independently of any assumptions about the conversion-dependent function. Based on Doyle's approximation [27], Flynn–Wall–Ozawa developed an alternative approach to calculate the activation energy:

$$\log(q) = \log\left[\frac{AE}{g(\alpha)R}\right] - 2.315 - \frac{0.457E}{RT} \tag{2}$$

where $g(\alpha)$ represents the integrated form of the conversion dependence function. This equation yields a more accurate value of the activation energy using iteration and the least-squares methods are adopted to improve the linear approximation to the temperature integration term. Both the Kissinger and the Flynn–Wall–Ozawa approaches assume that the DSC peak exotherm exhibits an iso-conversion and its value is independent of the heating rate. These two methods were adopted in this investigation herein using the data obtained in the dynamic heating experiments at various heating rates from 10 to 40 °C min^{-1}. Based on the Flynn–Wall–Ozawa and Kissinger methods and the observed maximum reaction rate peak in the DSC thermogram, the activation energy was obtained from the gradient of the line plotted in Fig. 2 for (a) soft epoxy/DDM and (b) OG/DDM. The calculated activation energies of the curing of the OG/DDM system are 31.19 and 36.30 kJ/mol according to the Kissinger and Flynn–Wall–Ozawa methods, respectively. The corresponding activation energies obtained for the curing of the soft epoxy/DDM are 51.60 and 56.09 kJ/mol, respectively. Table 1 summarizes the results. Hence, the soft epoxy/DDM system had a higher activation energy than the OG/DDM system, indicating that OG is more reactive than soft epoxy. However, the authors' earlier study [8] established that DGEBA/mPDA (48.21 KJ/mol (Kissinger) and 48.33 KJ/mol (Ozawa)) were more reactive than the OG/mPDA system (49.21 KJ/mol (Kissinger) and 51.95 KJ/mol (Ozawa)).

Curing conversion of soft epoxy/DDM/OG and DGEBA/mPDA/OG systems

The curing conversions of the soft epoxy/DDM/OG and DGEBA/mPDA/OG systems were determined from FTIR

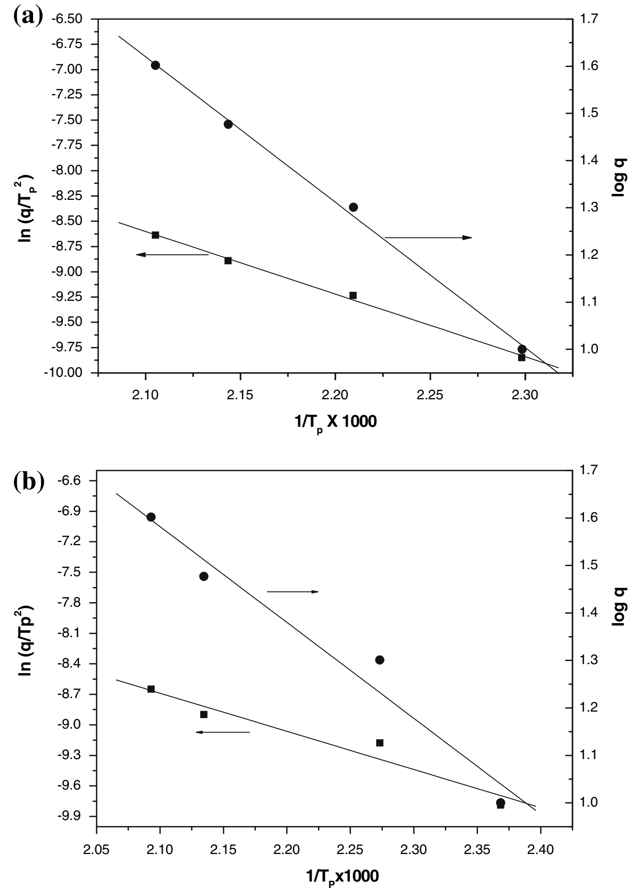


Fig. 2 Activation energies of curing obtained by Kissinger and Flynn–Wall–Ozawa (**a**) soft epoxy/DDM; (**b**) OG/DDM

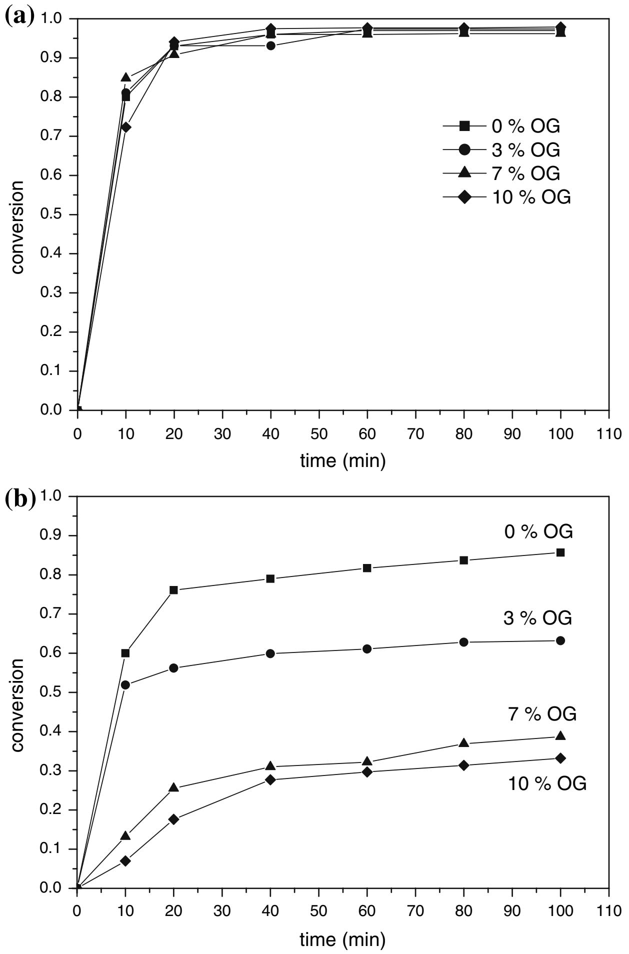


Fig. 3 Conversion of epoxy ring of two systems containing various OG (**a**) soft epoxy/DDM; (**b**) DGEBA/mPDA

spectra obtained at 120 °C. Figure 3a plots the conversion of epoxy, based on the $A_{910\ \mathrm{cm}^{-1}}/A_{829\ \mathrm{cm}^{-1}}$ of soft epoxy/DDM/OG while Fig. 3b is based on DGEBA/mPDA/OG at various times at a fixed temperature of 120 °C. $A_{910\ \mathrm{cm}^{-1}}$ [28] denotes the area under the absorption peak of the epoxy ring (epoxy and OG) and $A_{829\ \mathrm{cm}^{-1}}$ [28] is the area under the peak associated with the phenyl group. Figure 3a presents the epoxy conversion of soft epoxy/DDM/OG system at 120 °C for various periods. Soft epoxy/DDM with various OG contents exhibited high epoxy conversion (conversion > 0.95). Since the curing reaction of OG/DDM preceded that of soft epoxy/DDM, the severe aggregation that could be otherwise have been caused by the POSS units [8] was avoided because more curing agent than was required for the amount of OG was present, resulting in a high epoxy conversion. Figure 3b displays the epoxy conversion of DGEBA/mPDA/OG system at 120 °C over various periods. The T_g results reveal a high glass transition temperature (T_g = 127–155 °C) during the reaction at T = 120 °C. The system exhibits vitrification, resulting in OG aggregation in the epoxy matrix. Therefore, the extent of conversion of epoxy in the DGEBA/mPDA/OG system declined markedly as the OG content increased.

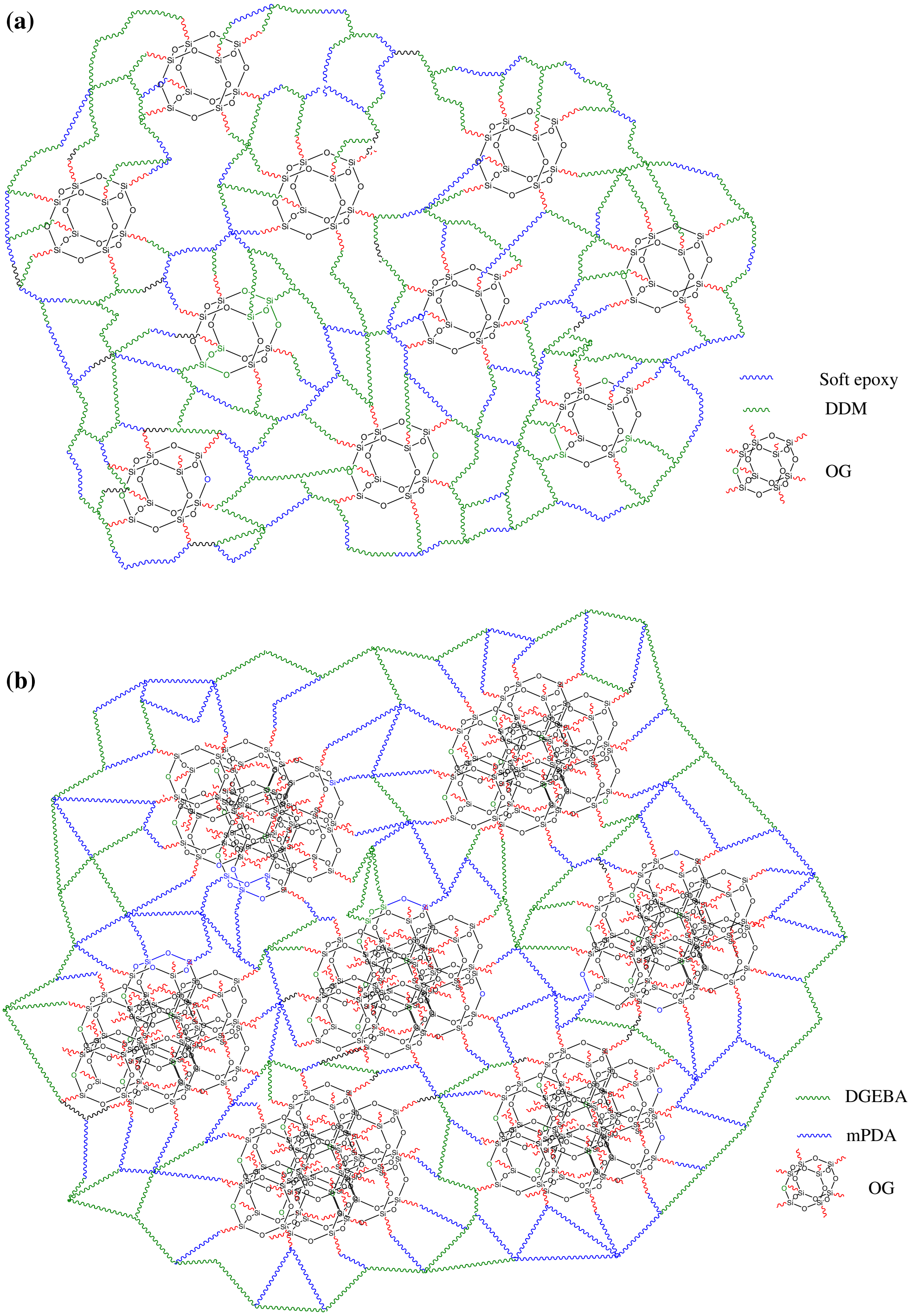
Table 1 Activation energies of dynamic curing reaction

	DGEBA/mPDA[a] (kJ/mol)	OG/mPDA[a] (kJ/mol)	Soft epoxy/DDM (kJ/mol)	OG/DDM (kJ/mol)
Kissinger	48.21	49.21	51.60	31.19
Flynn–Wall –Ozawa	48.33	51.95	56.09	36.30

[a] Ref. 8

Structural models of soft epoxy/DDM/OG and DGEBA/mPDA/OG systems

The results and discussions of the reactivity and conversion by the curing agent, epoxy and epoxy-POSS suggest a reasonable molecular structure of the epoxy/curing agent/epoxy-POSS system, which is presented as Scheme 1. Scheme 1a depicts a model of the structure of soft epoxy/DDM/OG system. Since OG is cured using DDM more rapidly than soft epoxy is cured with DDM and the amount of DDM exceeds that required to react with the soft epoxy, the OG does not aggregate and the dispersion of OG in the



Scheme 1 Structure model of OG dispersion in epoxy resin (**a**) soft epoxy/DDM/OG; (**b**) DGEBA/mPDA/OG

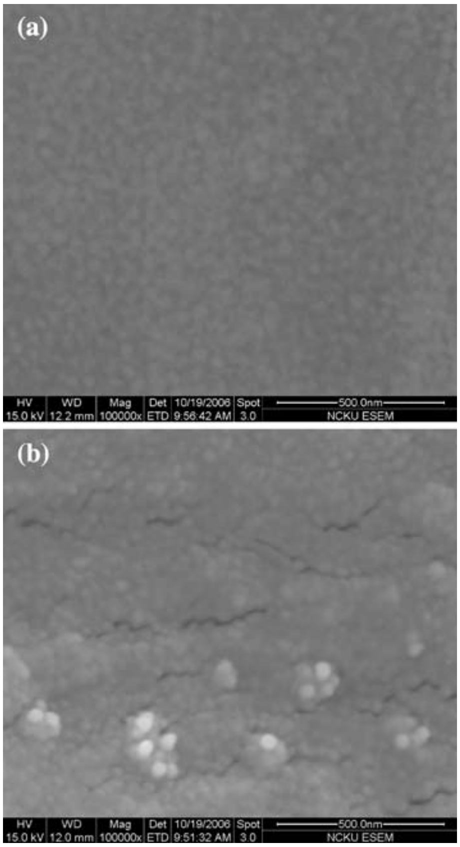


Fig. 4 Presents the ESEM of two systems containing OG 10 phr (**a**) soft epoxy/DDM; (**b**) DGEBA/mPDA

soft epoxy/DDM matrix is excellent. Figure 4a displays an ESEM micrograph of the soft epoxy/DDM/OG 10 phr system, which exhibits no POSS aggregation. The morphology of the soft epoxy/DDM/OG system was consistent with the structural model of soft epoxy/DDM/OG. Scheme 1b presents a structure model of the DGEBA/mPDA/OG system. The reactivity and epoxy conversion results for the DGEBA/mPDA/OG system indicated the severe aggregation of OG. When the DGEBA was cured with mPDA before OG/mPDA, the DGEBA/mPDA matrix shrunk, resulting in the aggregation of OG. Figure 4b shows an ESEM micrograph of DGEBA/mPDA/OG 10 phr, which reveals severe OG aggregation, explaining the decrease in the conversion of epoxy as the OG content in the in DGEBA/mPDA/OG system increases.

Conclusions

In this study, two epoxy resin systems (soft epoxy/DDM, DGEBA/mPDA) were modified using various amounts of octaepoxy POSS. The reactivity of the epoxy or OG that had been cured using the curing agent was utilized to verify the POSS dispersion state in the epoxy resin matrix. The dynamic curing kinetics indicated that the OG was more reactive with DDM than with the soft epoxy. The authors' previous work established that the curing reaction of DGEBA with mPDA occurred before that with OG.The dynamic curing kinetics herein indicate that the reactivities of the two epoxy systems that contain different amounts of octa-epoxies POSS exhibit different tendencies The different reactivities of these two systems reveal that soft epoxy/DDM/OG exhibits high epoxy conversion ($\alpha > 0.95$) and that DGEBA/mPDA/OG exhibits low epoxy conversion. The glass transition temperature (T_g) of the soft epoxy/DDM/OG system improved as the OG content increased, since the curing conversion is increased and the OG was better dispersed.

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