國立交通大學應用化學研究所
碩士論文

具八酚官能基之多面體聚矽氧烷於高分子作用力、奈米複合材料的合成與研究

The Syntheses and Studies of Octaphenol Polyhedral Oligomeric Silsesquioxane in Polymer Interactions and Nanocomposite

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Outline of Contents

Pages

Acknowledgments

Chapter 1 Introduction

Chapter 2 The syntheses of octaphenol-POSS

Chapter 3 Studies of hydrogen bonding in Blends of Phenolic resin with AS-POSS

Chapter 4. A Novolac type of phenolic nanocomposite from octaphenol-POSS

List of tables

Pages

List of figures

摘要

有機-無機混成材料結合了有機材料及無機材料的性質,而奈米級有機-無機複合材料由於可大幅補強原材料的性質,在近年引起相當廣泛的研究。在眾多奈米級填充物中,多面體聚矽氧烷由於具備固定的籠狀結構而有良好的尺寸安定性,在矽原子上連接之有機官能基可藉由傳統有機合成方法加以改質,來達成與高分子間有良好的作用力而在分子等級分散均勻。本論文以含八酚官能基的多面體聚矽氧烷爲研究主體,內容則分爲以下三大主題:

(1) 含八酚官能基的多面體聚矽氧烷之合成

合成產物均藉由紅外線光譜以及核磁共振光譜做出證實。

(2) octa(acetoxystyryl)- octasilsesquioxane (AS-POSS)與酚醛樹酯混摻之高分子間作用力研究

高分子之相容性和特殊作用力的探討有助於解釋許多高分子的行爲。本研究乃利用 AS-POSS 其有機部份可產生氫鍵受體,可與其他帶有氫鍵予體的高分子產生氫鍵作用力,藉此探討酚醛樹酯與多面體聚矽氧烷間的氫鍵作用情形。

(3) 利用含八酚官能基的多面體聚矽氧烷改質酚醛樹酯,以製備有機-無機混成奈米複合材料

酚醛樹酯由於其良好的機械強度、耐熱性以及尺寸穩定性,從工業上到太空科技上均具有廣泛的用途。本研究乃利用酚醛樹酯聚合過程中摻入含八酚官能基的多面體聚矽氧烷,使得奈米粒子與高分子之間產生反應藉以達成製備奈米複合材料,令改質後的酚醛樹酯性質能夠進一步提升之目的。

Abstract

Inorganic-organic hybrid materials combine both properties of inorganic and organic materials, and inorganic-organic hybrid nanocomposites have attracted enormous interests due to their large improvement of material properties. In numerous nanofillers, polyhedral oligomeric silsesquioxane(POSS) compounds have good dimension stability because they embody a truly hybrid (inorganic-organic) architecture, which contains an inner inorganic framework made up of silicone and oxygen $(SiO_{1.5})_x$, that is externally covered by organic substituents. A selection of POSS nanostructured chemicals now exist that contain various combinations of nonreactive substituents and/or reactive functionalities. Thus, POSS nanostructured chemicals may be easily incorporated into common plastics via copolymerization, grafting, or blending to achieve well dispersion. In this thesis, we focus on three major subjects which based on octaphenol-polyhedral oligomeric silsesquioxane:

(1) The syntheses of octaphenol-POSS

The synthesis products are confirmed by FTIR and NMR.

(2) Studies of hydrogen bonding in blends of phenolic resin with octa(acetoxystyryl)- octasilsesquioxane AS-POSS

We concentrate on the polymer miscibility and specific interaction, especially in the hydrogen bonding interaction. The AS-POSS contains carbonyl group that is known as a proton acceptor for several polymers with proton doner, we can study the hydrogen bonding between phenolic and AS-POSS.

(3) A novolac type of phenolic nanocomposite from octaphenol-POSS

Phenolic resins are preferred in a wide range of applications, from commodity and construction materials to high technology aerospace industry. This recognition emerges from the fact that these resins have several desirable characteristics, such as superior mechanical strength, heat resistance and dimensional stability. In this studies, we incorporated octaphenol-POSS into phenolic matrix by copolymerization to attain further improvement of thermal properties.

Chapter 1 Introduction

1.1 A quick history of Polyhedral Oligomeric Silsesquioxane(POSS)

In 1991, Lichtenhan and the Air Force Research Laboratory received funding from the Air Force Office of Scientific Research (AFOSR) for his proposed development of POSS macromers containing a polymerizable functional group and the subsequent synthesis of a POSS-copolymer[1,2]. The University-Government collaboration between Lichtenhan and Feher rapidly expanded to include more academic coaborators including Laine and Sellinger[3], Mather et al.[4] and others who were all intrigued by the physical and mechanical property improvements imparted by incorporation of these nanostructured materials into polymer systems. In the late nineties not only was government and academic interest growing, but also that of the industrial sector which desired lowers costs and larger quantities of the material.

The fall of 1998 marked the start-up of Hybrid Plastics in Fountain Valley, CA, which transitioned the government scale-up facilities to the commercial sector through a cooperative research and development agreement. In addition, the award of a 3 year multimillion dollor NIST Advanced Technology Program grant in 1998 to Hybrid Plastics was critical in both reducing the prices of the POSS feedstocks and macromers (\$ 5000- \$ 10000 down to \$ 50- \$ 2000 per pound) and increasing production (<20 to >2000 lb/year) to satify the more than 100 companies now investigating how the incorporation of POSS improves material properties for their applications. In the summer of 2003, Hybrid Plastics launched critical agreements with Southern Mississippi State University and the City of Hattiesburg for their development of a 26000 sq ft production facility and a 1500 sq ft R&D center.

The nearly exponential increase in the number of academic researchers, academic publications (Fig. 1-1), government programs, and industrial research efforts on POSS nanostructured chemicals has made it one of the top nanomaterials in the nanoscience/nanotechnology field. Indeed, the versatility of the POSS molecule, the more than one hundred demonstrated compatible polymer systems and the innumerable applications makes it difficult to understand and discern the current and future direction. However, it is clear that at least one concerted effort with a single-minded goal of predicting and controlling structure-property relationships is needed, and os beong pursued by a number of research groups working with POSS nanostructured chemicals.

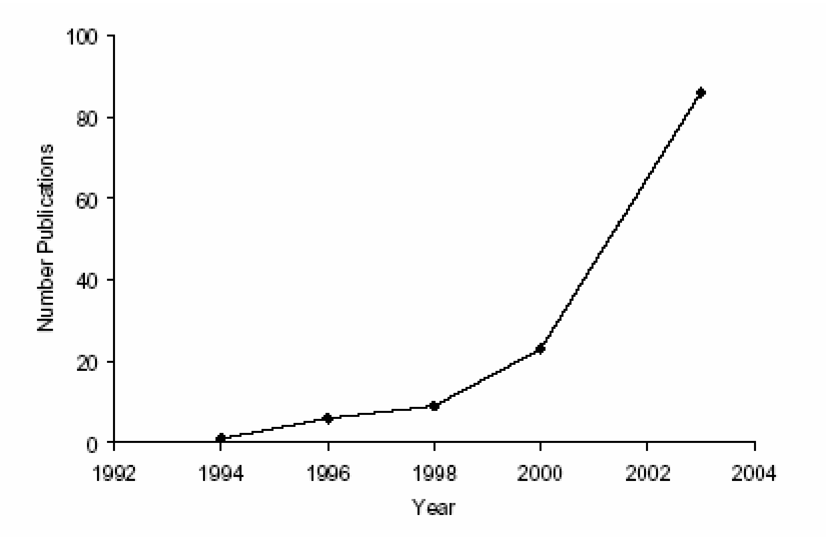

Fig. 1-1. Plot of the number of POSS publications versus the year in which they were published.

1.2 Silsesquioxanes and Polyhedral Oligomeric Silsesquioxane(POSS)

The term silsesquioxane refers to all structures with the empirical formula $RsiO_{1.5}$, where the R is hydrogen or any alkyl, alkylene, aryl, arylene, or organofunctional derivative of alkyl, alkylene, aryl, or arylene groups. The silsesquioxanes include random structures, ladder structures, cage structures, and partial cage structures, as illustrated in Figure 1-2 [5].

In 1995, Baney et al. reviewed the structure, preparation, properties, and applications of silsesquioxanes, especially the ladder-like polysilsesquioxanes shown in Figure 1-2 (structure b). These include poly(phenylsilsesquioxane) (PPSQ) [6,7], poly(methyl silsesquioxane) (PMSQ) [8-10], and poly(hydridosilsesquioxane) (PHSQ)

[11,12]. These ladder-like polymers have an outstanding thermal stability and they exhibit oxidative resistance even at temperatures of more than 500℃. In addition, these ladder-like polymers have good insulating properties and gas permeabilities.

Therefore, the ladder-like silsesquioxane polymers have a variety of applications in areas such as photoresist coatings [13,14] for electronics and optical devices, interlayer dielectrics and protective coating films [15,16] for semiconductor devices, liquid crystal display elements [17], magnetic recording media [18], optical fiber coatings [19], gas separation membranes [20], binders for ceramics [21]. However, in the past few years, much more attention has been paid to the silsesquioxanes with specific cage structures [Figure 1-2 structure c-f]. These Polyhedral Oligomeric Silsesquioxane have been designated by the abbreviation POSS.

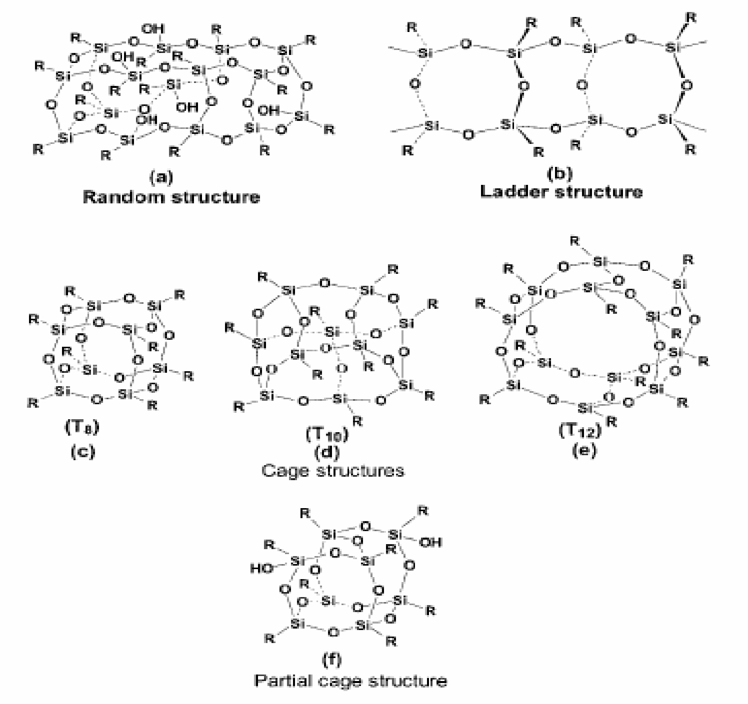

Fig. 1-2. Structures of silsesquioxanes.

POSS compounds embody a truly hybrid (inorganic-organic) architecture, which contains an inner inorganic framework made up of silicone and oxygen $(SiO_{1.5})_x$, that is externally covered by organic substituents. These substituents can be totally hydrocarbon in nature or they can embody a range of polar structures and functional groups. POSS nanostructured chemicals, with sizes of from 1 to 3 nm in diameter, can be thought of as the smallest possible particles of silica, as shown in Figure 1-3. They may be viewed as molecular silicas. However, unlike silica, silicones, or fillers, each POSS molecule contains organic substituents on its outer surface that make the POSS nanostructure compatible with polymers, biological systems, or surfaces. Furthermore, these groups can be specially designed to be nonreactive or reactive.

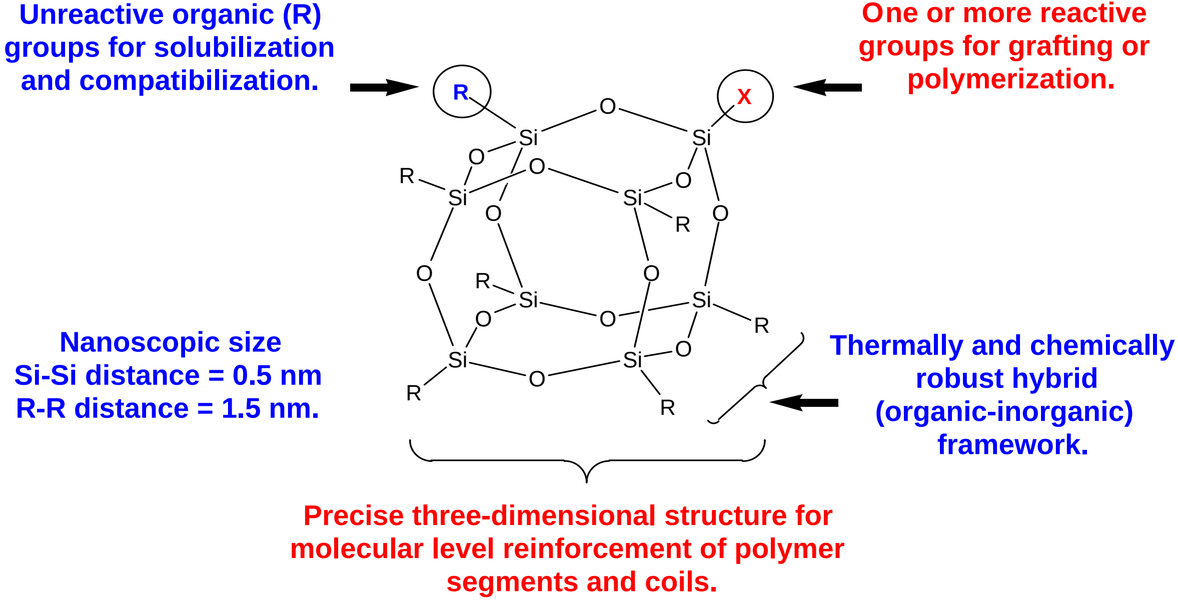

Fig. 1-3. Structure of POSS

A variety of POSS nanostructured chemicals have been prepared which contain one or more covalently bonded reactive functionalities that are suitable for polymerization, grafting, surface bonding, or other transformations [22]. Unlike traditional organic compounds, POSS chemicals release no volatile organic components, so they are odorless and environmentally friendly.

The incorporation of POSS derivatives into polymeric materials can lead to dramatic improvements in polymer properties which include, but are not limited to, increases in use temperature, oxidation resistance, surface hardening, and improved mechanical properties, as well as reductions in flammability, heat evolution, and viscosity during processing. These enhancements have been shown to apply to a wide range of thermoplastics and a few thermoset systems [23]. It is especially convenient that the use of POSS monomers doesn't require dramatic changes in processing. Monomers are simply mixed and copolymerized. As long as the POSS monomer is soluble in the monomer mixture, it is incorporated in a true molecular dispersion into the copolymer. No phase separation will occur although some aggregation of POSS units bound with polymer will occur. This is a significant advantage over current filler technologies. POSS nanostructures have also shown significant promise for use in catalyst supports and biomedical applications as scaffolds for drug delivery, imaging reagents, and combinatorial drug development.

1.3 Polymer miscibility and interactions

Polymer blend phase behavior can be predicted or analyzed by inserting the binary interaction model into the thermodynamic framework of either the Flory-Huggins theory or an appropriate equation-of-state theory. It is useful for evaluation of isothermal phase boundaries, miscibility maps, or phase separation by using the simplicity of the Flory-Huggins theory and equation-of-state. Recently, several polymer theoretical equations of state are available [24], and some have been applied to polymer solutions and blends [25]. However, the role of polymer interaction in determining the phase behavior of polymer blends is fascinating from a number of concerns. Polymer interactions are usually meaning "strong" specific, and orientation dependent. In polymer blends, most of it have been widely concerned with the following intermolecular or inter-segment forces:

(a) Strong dipoles

(b) Hydrogen bonds

(c) Charge transfer complexes

(d) Ionic interactions in ionomers

Polymer miscibility is based on the assertion that the free energy of mixing can be written in the following form:

$$\frac{\Delta G_N}{RT} = \frac{\Phi_1}{N_1}\ln \Phi_1 + \frac{\Phi_2}{N_2}\ln \Phi_2 + \Phi_1 \Phi_2 \chi_{12} + \frac{\Delta G_H}{RT} \qquad (1\text{-}1)$$

The segmental interaction parameter χ is the “physical” interaction parameter and subscripts 1 and 2 refer to the blend components, while the ΔG_H term reflects free energy changes corresponding to specific interactions, most commonly, but not necessarily, hydrogen bonds. Nevertheless, hydrogen bonds are not easily characterized. There are two common experimental ways being able to characterized hydrogen bonds within polymers:

(a) Thermodynamic: Measurements depend upon thermodynamic changes in a system as a whole and can be related to molecular properties through the analyses of statistical mechanics, and these results are often model dependent and sensitive to various assumptions that have to made.

(b) Spectroscopic: Spectroscopy techniques can aid in the evolution of miscibility, specifically when the interactions induce a change in the material physical properties (e.g. glass transition temperature); such as a change can be measured by radiate energy, including spectroscopy of solid-state or liquid nuclear magnetic resonance (NMR), Fourier transform infrared spectroscopy (FTIR), Raman, XPS and others.

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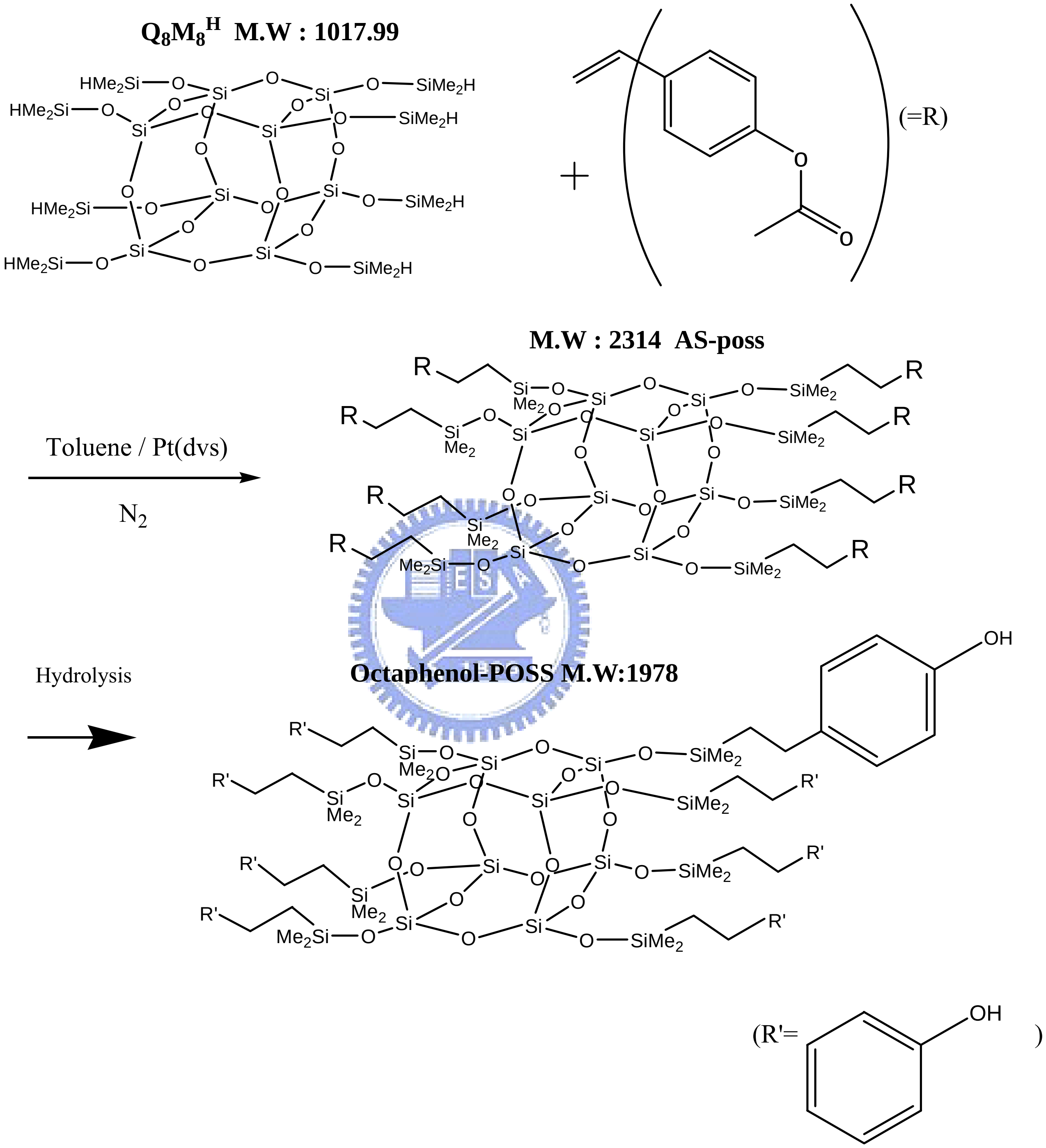
Chapter 2 The syntheses of octaphenol-POSS



Scheme 2-1. The syntheses of octaphenol-POSS

2.1 Experimental section

Materials

$Q_8M_8^H$ was purchased from Hybrid Plastics Co. Platinum divinyltetramethyldisiloxane complex, Pt(dvs) and acetoxystyrene were obtained from Aldrich Chemical Co. Inc. Octa(acetoxystyryl) octasilsesquioxane(AS-POSS) was synthesized as following method.

Synthesis of Octa(acetoxystyryl)octasilsesquioxane(AS-POSS)

$Q_8M_8^H$ (2.00 g, 1.96 m-mole) was placed in a 100 mL Schlenk flask equipped with a reflux condenser and a magnetic stirrer. Toluene (20 mL) was added to dissolve the cube, followed by the addition of 4-acetoxystyrene(3.2 g, 19.6 m-mole). Pt(dvs) (2 mM solution, 0.2ml) was added via a syringe. The reaction mixture was then heated to 80℃ under nitrogen and was completed in 4 hours. The solution was removed from Toluene under reduced pressure, then was dried in a vacuum oven at 80 ℃ for 24 hours. The product(3.17 g, 93 %), octa(acetoxystyryl)octasilsesquioxane (AS-POSS) was obtained. The AS-POSS is a colorless, viscous liquid, soluble in THF, $CHCl_3$, acetone, etc.

Synthesis of Octa(phenol)octasilsesquioxane(octaphenol-POSS)

AS-POSS(3.17g, 1.82mmole) was placed in a 100ml Schlenk flask with a magnetic stirrer. THF(20ml) was added to dissolve the liquid, followed by $NaOH_{(aq)}$(20ml, 10wt%). The reaction was carried out in room temperature under nitrogen and was complete in 2 days. Ethyl ether(20ml) and deionized water(20ml) was added to the solution, and then slowly added aqueous hydrochloric acid(10wt%) with stirring until pH=8. Two layers were formed. The top layer containing the product, octaphenol-POSS, was recovered. Residual ethyl ether and water were removed under vacuum. Octaphenol-POSS(2.26g, 65%) is a light brown, viscous liquid, soluble in THF, benzene, $CHCl_3$, etc.

2.2 FTIR and NMR spectrum of the products

2.2.1 Characterizations

***Nuclear magnetic resonance* (^{1}H NMR)**

^{1}H NMR spectra were recorded on a Varian Unity Inova 500 FT NMR Spectrometer operating at 500 MHz with chemical shift reported in parts per million(ppm). Deuterium chloroform was used as solvent.

***Fourier Transform Infrared Spectroscopy* (FTIR)**

Infrared spectroscopic measurements were recorded on a Nicolet Avatar 320 FTIR spectrophotometer, and 32 scans were collected with a spectral resolution of 1 cm^{-1}. Infrared spectra of polymer blend films were determined with the conventional NaCl disk method. All sample preparations were under continuous nitrogen flow to ensure minimal sample oxidation or degradation. Samples were prepared by casting the THF solution directly onto a NaCl disk and dried under conditions similar to those used in the bulk preparation.

2.2.2 Discussions

The FTIR spectra of $Q_8M_8^H$, acetoxystyrene, and the final hydrosilylation product, AS-POSS, are shown in Figure 2-1. The strong absorption peak at 1100 cm^{-1} of $Q_8M_8^H$ and AS-POSS is the vibration of the siloxane (Si-O-Si) group, the feature of the POSS. The characteristic stretching vibration peaks of vinyl (φ-CH=CH$_2$) and Si-H groups are at 1650 and 2200 cm^{-1}, respectively. In AS-POSS, the peaks for Si-H and the vinyl groups have disappeared completely, indicating that the complete reaction was obtained. Furthermore, the carbonyl group at 1765 cm^{-1} of acetoxystyrene remained in AS-POSS, is another evidence of the successful attachment of the acetoxystyrene on the POSS. In octaphenol-POSS, the broad band of hydroxyl group appeared at 3400 cm^{-1} and the sharp peak of cabonyl group at 1765 cm^{-1} disappeared, indicated that the hydrolysis reaction is completed. Figure 2-2 and 2-3 shows the ^1H NMR spectra of the AS-POSS and octaphenol-POSS, respectively. Clearly, the peaks for the chemical shifts of vinyl protons around 5.8 ppm and the Si-H protons at 4.7 ppm are both disappeared, also indicating the complete reaction. The vinyl groups of acetoxystyrene is able to attach the Si-H bond of $Q_8M_8^H$ on either α or β carbon, therefore, the spectrum shown in Figure 2-2 and 2-3 are the mixture of these two possible structures. From the integrated areas of these two methyl groups attach on Si, it is able to estimate that the ratio of the integrated areas of carbon 1:1’ is approximately 3:1. That means the α carbon attachment is three times of the β carbon attachment.

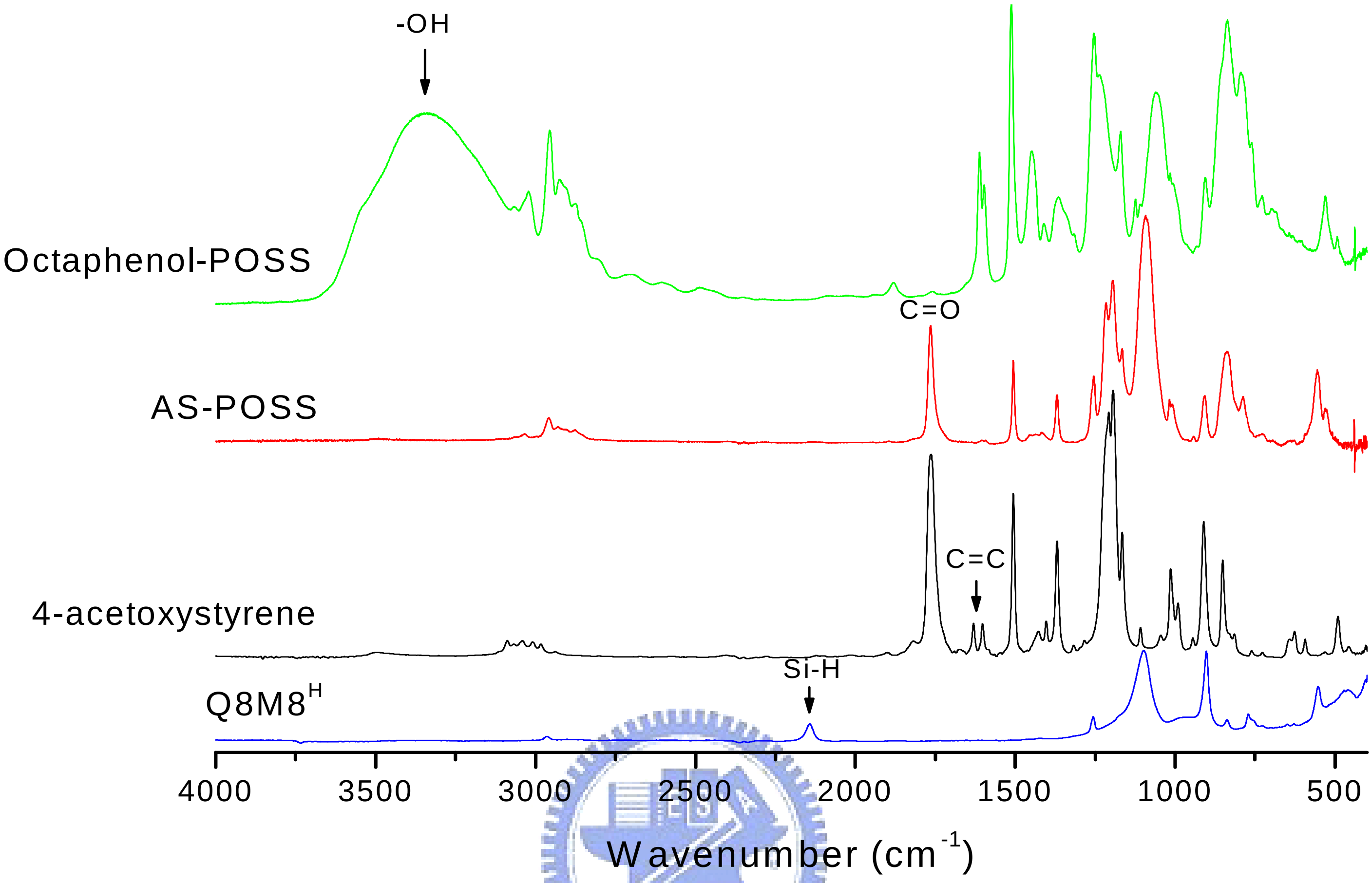


Fig. 2-1. FTIR spectrum of the synthesis process

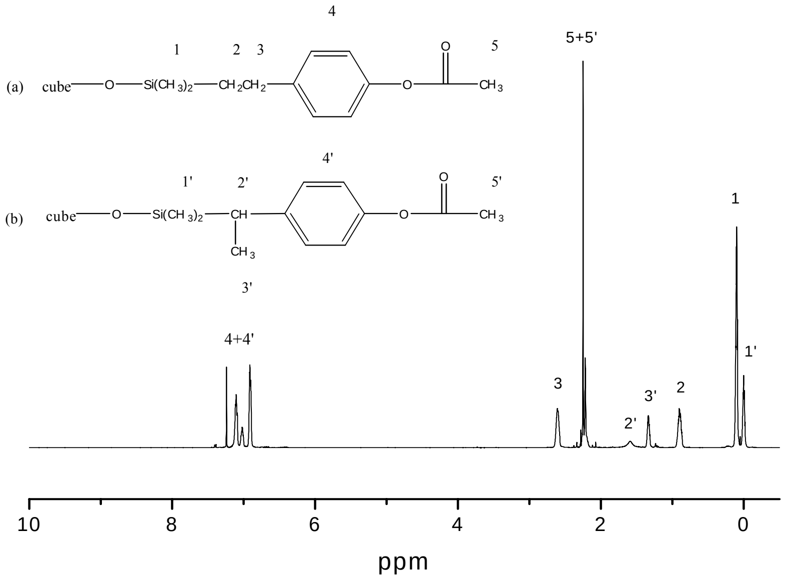


Fig. 2-2. NMR spectrum of AS-POSS

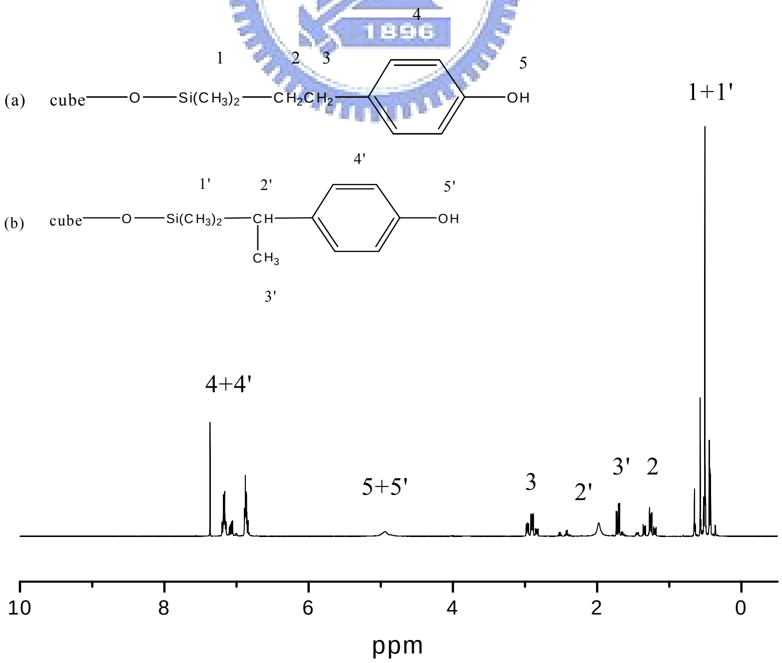


Fig. 2-3. NMR spectrum of octaphenol-POSS

Chapter 3 Studies of hydrogen bonding in Blends of Phenolic resin with AS-POSS

Abstract

We have successfully synthesized a polyhedral oligomeric silisesquioxane (POSS) containing eight acetoxystyryl functional groups [octa(acetoxystyryl)-octasilsesquioxane (AS-POSS)] and then blends with the phenolic resin to form nanocomposites through the hydrogen bonding interaction between the phenolic hydroxyl group and the AS-POSS carbonyl group. Infrared spectroscopy analyses provide positive evidence for this type of hydrogen-bonding interaction. In addition, the inter-association equilibrium constant based on Painter-Coleman association model (PCAM) between phenolic resin and POSS can be indirectly calculated from the fraction of hydrogen-bonded carbonyl groups and quantitative analyses show that the hydroxyl-siloxane inter-association from PCAM is exactly consistent with the classical Coggeshall and Saier (C&S) methodology.

3.1 Introduction

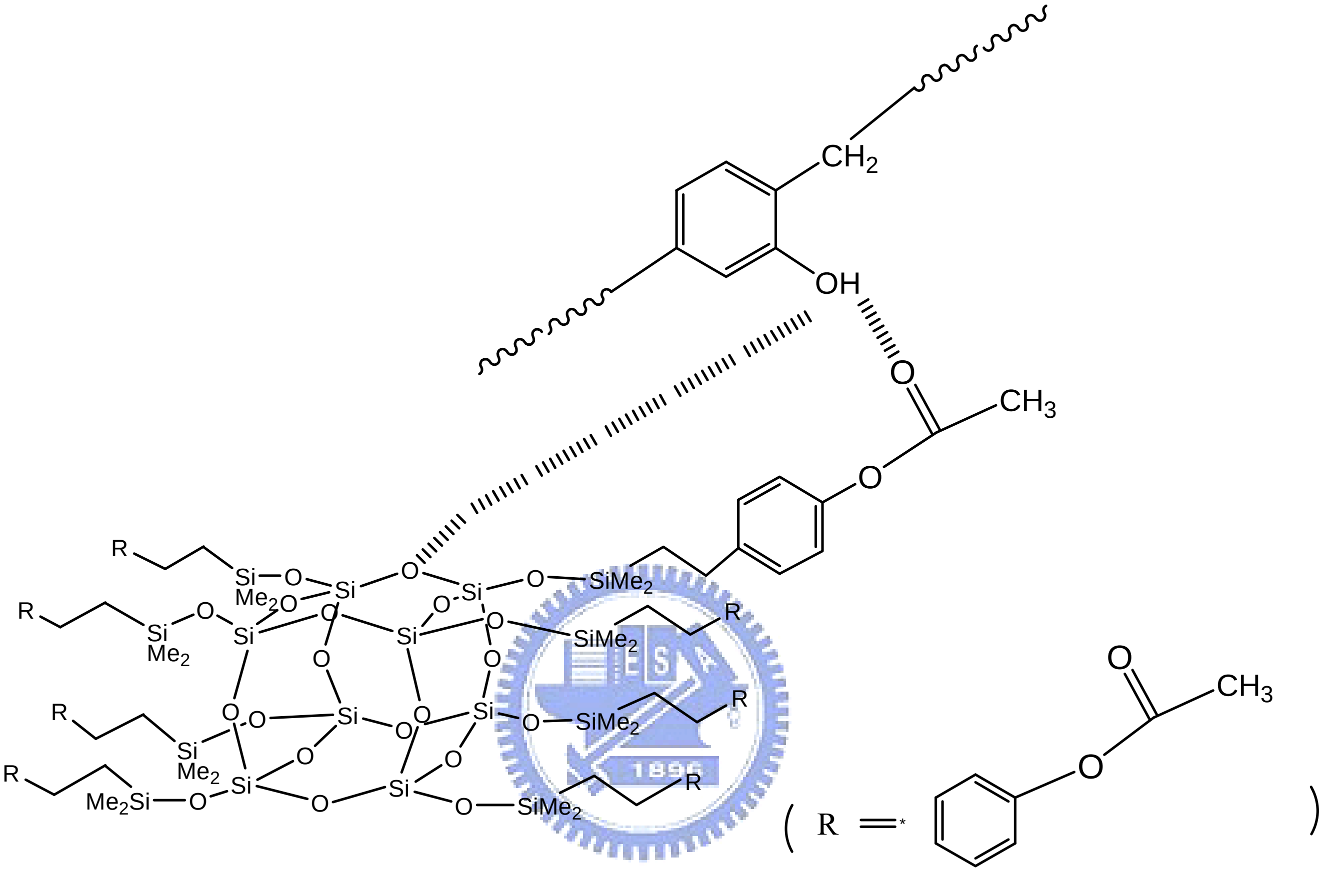
Incorporation of nanoparticles into polymer matrixes to enhance polymer properties has attracted enormous interests in recent years due to its potential as candidate materials for bridging the gap between polymer and nanoparticles. In particular, polyhedral oligomeric silsesquioxanes (POSS) offer one solution to this need since they embody an inorganic-organic hybrid architecture with a well-defined inorganic framework composed of silicone and oxygen $(SiO_{1.5})_x$ and organic substituents containing nonreactive or reactive functionalities. By designing the functionality of the organic substituents, it is possible to create octafunctional or monofunctional macromonomers at desired usage. Therefore, these nanostructured chemicals can be incorporated easily into polymer chains through copolymerization, such as polysiloxane [1], poly(methyl methylacrylate) [2-3], poly(styrene) [4], epoxy [5], polyurethane [6], polyimide [7], and polynorborbornene [8].

Physical properties of polymer/POSS nanocomposites are strongly influenced by the miscibility between the host polymer and the POSS moiety. Random copolymerization by the organic functional groups of the POSS is one approach to attain this end. Therefore, in our previous study [9], we have synthesized a series of poly(vinylphenol-co-vinylpyrrolidone-co-POSS) (PVPh-co-PVP-co-POSS) copolymers, resulting in significant glass transition temperature increase than the corresponding non-POSS PVPh-co-PVP copolymer due to the strong hydrogen bonding existing between the PVPh and the POSS. The synthesis of a random copolymer is more complicated and time-consuming than a blend. Therefore, polymer blending is a more convenient method to prepare the polymer/POSS nanocomposites. Since the combined entropy contribution to the free energy in mixing two polymers is negligibly small, specific intermolecular interactions are generally required for the miscibility of polymer blends. To improve the properties and miscibility of hybrid materials, it is necessary to ensure that favorable specific interactions exist between these components, such as hydrogen bonding [10], dipole–dipole interactions, and acid–base complexation.

Our previous study [11], indicated that a simple blending of POSS containing nonreactive or inert diluent functional groups (here is octaisobutyl POSS) with phenolic resin did not give satisfactory results because of poor miscibility. The inter-association equilibrium constant between the phenolic hydroxyl group and the octaisobutyl POSS siloxane group (38.6) is lower than the self-association equilibrium constant of the pure phenolic (52.3) based on the Painter-Coleman association model (PCAM) [10]. This result indicates that the POSS tends to partial miscible with phenolic in the phenolic/POSS hybrid due to poor interaction between the phenolic resin and the octaisobutyl POSS. Functionalization of the POSS to possess hydrogen bonding acceptor pedant groups is expected to improve the miscibility with phenolic resin. Functionalization of $Q_8M_8^H$ $[HsiMe_2OsiO_{1.5}]_8$ can be achieved by the hydrosilylation reaction of Si-H groups in the presence of a platinum catalyst with acetoxystyrene. The hydrogen bonding interaction between the carbonyl group of the poly(acetoxystyrene) (PAS) and the hydroxyl group of the phenolic resin has widely investigated via infrared and solid state NMR in our previous studies [12]. We found that the inter-association equilibrium constant for the phenolic/PAS blend (64.6) is higher than the self-association equilibrium constant of pure phenolic (52.3), implying that the tendency toward hydrogen bonding of the phenolic resin and PAS dominates the self-association (intra-hydrogen bonding) of the phenolic resin in the mixture.

By infrared (FTIR) spectroscopy, the carbonyl, hydroxyl and siloxane vibration have been proved to be the excellent tool to detect these molecular interactions [13]. This tool can be used to study the mechanism of interpolymer miscibility through the formation of different type hydrogen bonds both qualitatively and quantitatively. However, the inter-association equilibrium constant between the phenolic hydroxyl group and the POSS siloxane group can not be quantified directly because no carbonyl group is available to measure the fraction of the hydrogen bonded group from IR analysis in this binary blend. The siloxane-stretching mode near 1100-1200 cm^{-1} is a highly coupled mode that is conformationally sensitive and can not be readily decomposed into two peaks, corresponding to the free and the hydrogen-bonded siloxane absorptions. Therefore, according to our previous study [11], the inter-association equilibrium constant (K_A) between hydroxyl group of phenolic resin and siloxane group of octaisobutyl POSS was calculated by using classical Coggeshall and Saier (C&S) [14] methodology. However, the inter-association equilibrium constant obtained from low molecular weight compound is not exactly the same as that from the true polymer blend due to the intramolecular screening and functional group accessibility effects in the miscible polymer blend [15]. Fortunately, in our previous study [11], the octaisobutyl POSS is the low molecular weight compound, thus this calculation can be considered as the true inter-association equilibrium constant between the phenolic hydroxyl group and the POSS siloxane group. To recheck the inter-association equilibrium constant between the phenolic hydroxyl group and the POSS siloxane group in the present study, the K_A value is determined indirectly from a least square fitting procedure of the experimental fraction of hydrogen bonded carbonyl group of the AS-POSS in this binary blend. We found that the inter-association equilibrium constant of hydroxyl-siloxane have good correlation between these two methods. The hydrogen bonding formation is shown as scheme 3-1.

3.2 Experiment section



Scheme 3-1. Hydrogen bonding formation of blends of phenolic and AS-POSS

Materials

The phenolic used in this study was synthesized with sulfuric acid via a condensation reaction and gave average weights of M_n=500 and M_w=1200. Octa(acetoxystyryl) octasilsesquioxane(AS-POSS) was synthesized as mentioned before..

Blend Preparation

Blends of phenolic/AS-POSS of various compositions were prepared by solution blending. Tetrahydrofuran solution containing 5 wt% of the mixture was stirred for 6-8 h, and then the solvent was evaporated slowly at room temperature for 1 day. To ensure total elimination of solvent, the powder of the blend was then dried in a vacuum oven at 60 ℃ for 2 days.

3.3 Results and Discussion

In our previous study [11], we have discussed in details the hydrogen bonding interaction between the phenolic hydroxyl groups and the POSS siloxane groups using 1D and 2D FTIR spectra. Figure 3-1(a) shows the infrared spectra in the range from 2700 cm^{-1} to 4000 cm^{-1} of the pure phenolic and various phenolic/AS-POSS nanocomposites measured at room temperature. The pure phenolic polymer exhibits two bands in the hydroxyl stretching region of the infrared spectrum. A very broad band centered at 3350 cm^{-1} is attributed to the wide distribution of the hydrogen bonded hydroxyl group while a narrower shoulder band at 3525cm^{-1} is caused by the free hydroxyl group. Figure 3-1(a) clearly shows that the intensity of the free hydroxyl absorption (3525cm^{-1}) decreases gradually as the AS-POSS content of the blend is increased from 5 to 90 wt%. The hydrogen-bonded hydroxyl band in the phenolic tends to shift into a higher frequency with increasing AS-POSS content at the vicinity of 3465 cm^{-1}. This change is due to the switch from the hydroxyl-hydroxyl bond to the hydroxyl-carbonyl or hydroxyl-siloxane bond.

Figure 3-1(b) displays the infrared spectra in the region from 1680 cm^{-1} to 1820 cm^{-1} for various phenolic/AS-POSS blend compositions measured at room temperature. The carbonyl stretching frequency is split into two bands at 1760 cm^{-1} and 1735 cm^{-1}, corresponding to the free and the hydrogen-bonded carbonyl groups, respectively. The band can be easily decomposed into two Gaussian peaks, with areas corresponding to the hydrogen-bonded carbonyl (1735cm^{-1}) and free carbonyl (1760cm^{-1}) as shown in Figure 3-2. In order to obtain the fraction of the hydrogen-bonded carbonyl, the known absorptivity ratio for hydrogen bonded and free carbonyl contributions is required. We have employed a value of $\alpha_{HB}/\alpha_F=1.5$, which was previously calculated by Moskala et al. [10]. Fractions of hydrogen bonded carbonyl through curve fitting are summarized in Table 3-1, indicating that the hydrogen bonded fraction of the carbonyl group increases with the increase of the phenolic content.

Table 3-1: Curve fitting of the area fractions of the carbonyl stretching bands in the FTIR spectra of phenolic/AS-POSS blends recorded at room temperature.

Phenolic/AS-POSS Wt Ratio	Free C=O			H-Bonding C=O			fB_{bPB}^{*P}
	ν, cmP^{-1P}	$WB_{1/2B}$, cmP^{-1P}	AB_{fB} %	ν, cmP^{-1P}	$WB_{1/2B}$, cmP^{-1P}	$AB_{b B}$%	
0/100	1763.2	23.5	100	-	-	-	-
10/90	1765.2	18.2	52.6	1739.3	29.3	47.4	37.5
20/80	1764.8	16.5	41.5	1737.3	28.0	58.5	48.4
30/70	1764.5	17.0	36.1	1735.5	27.8	63.9	54.1
40/60	1763.4	16.3	32.6	1733.5	26.3	67.4	58.0
50/50	1763.6	16.9	29.9	1733.6	26.3	70.1	61.0
70/30	1762.8	17.0	25.6	1732.1	25.5	74.4	66.0
80/20	1762.1	18.0	23.3	1731.3	24.7	76.7	68.8
90/10	1762.5	18.6	22.1	1731.0	25.3	77.9	70.1

ν: wavenumber, $W_{1/2}$: half width, *f_b: fraction of hydrogen bonding interaction

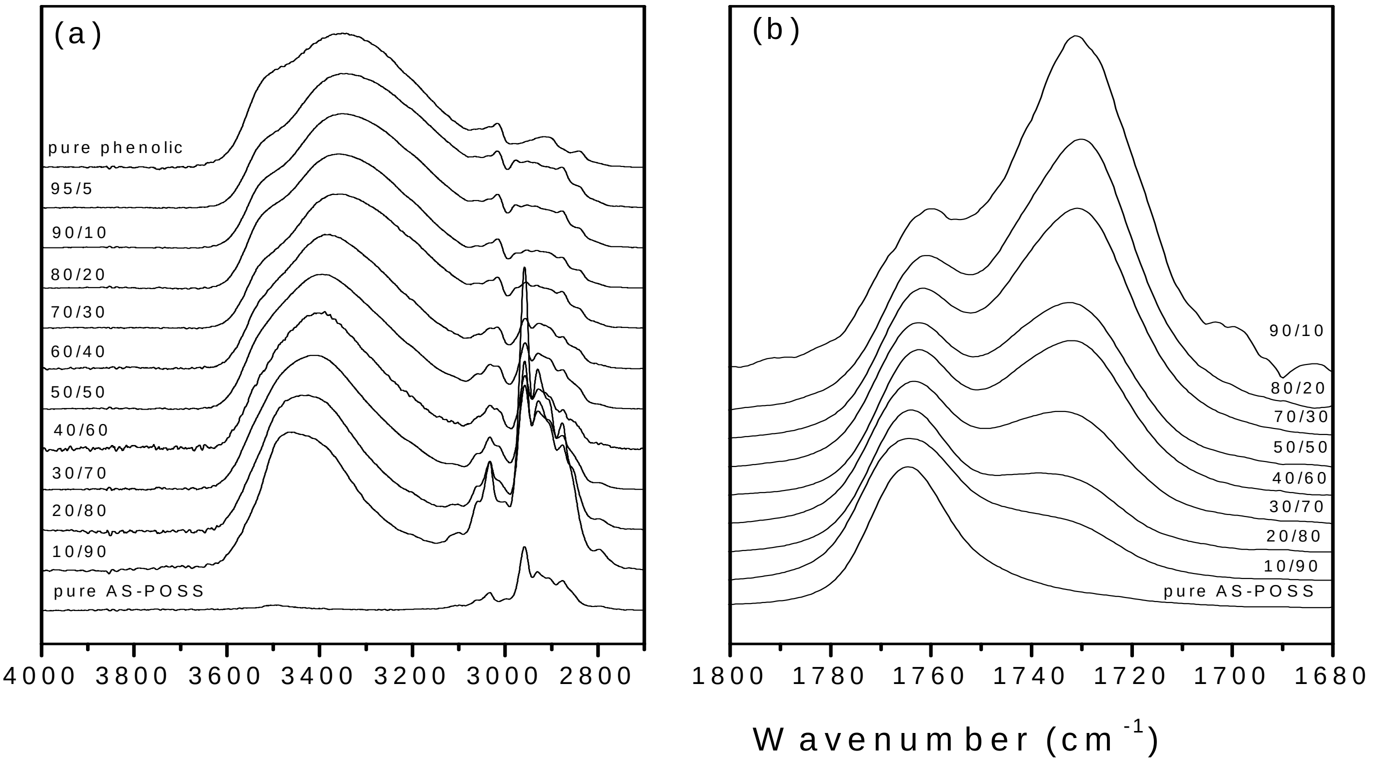


Fig. 3-1 Infrared spectra of phenolic/AS-POSS blend at room temperature in the hydroxyl stretching region (a) and carbonyl stretching region (b).

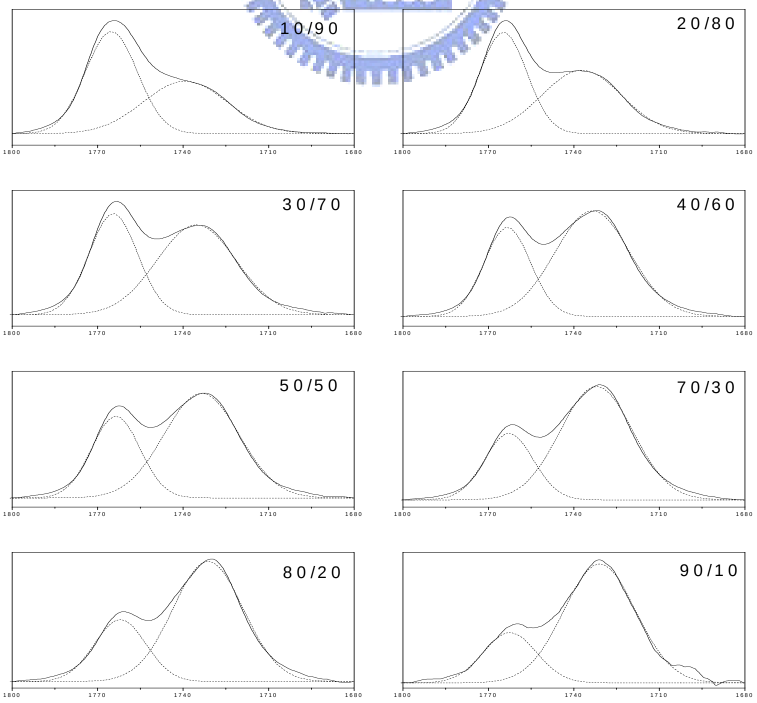


Fig. 3-2 Deconstructed models of the carbonyl stretching bands (in Figure 2) of the weight percent of phenolic/AS-POSS blends at various compositions.

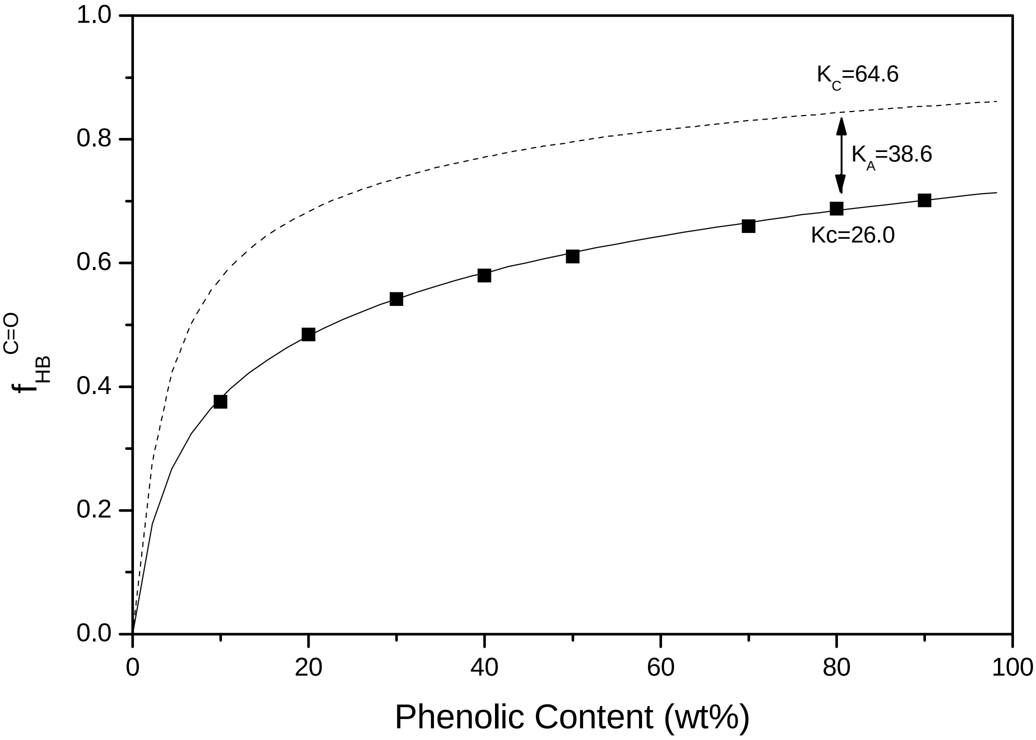


Fig. 3-3 Fraction of the hydrogen-bonded carbonyl group versus composition: (■)FT-IR data, (--) theoretical values from phenolic/PAS blend (K_A=64.6) and (—) theoretical values from phenolic/AS-POSS (K_A=26.0)

Figure 3-3 shows plots of the experimental data and theoretical predicted curve as a function of composition at room temperature that demonstrates the ability of PCAM to predict the degree of hydrogen bonding on the carbonyl group. Figure 3-3 indicates that the experimental values are generally lower than the predicted values based on using K_A = 64.6 from phenolic/PAS blends. This result also indicates that the hydroxyl groups of phenolic not only interact with the carbonyl group of the acetoxystyrene but also with the siloxane group of the POSS, which is consistent with results from our previous study [11]. In other words, the AS carbonyl competes with the siloxane of POSS to form a hydrogen bond with hydroxyl groups of the phenolic resin. The numerical method is employed to determine K_A of the phenolic/AS-POSS blend according to the PCAM based on the fraction of the hydrogen bonded carbonyl group. The approximate equations are [11]:

$$\Phi_B = \Phi_{B1}\Gamma_2\left[1 + \frac{K_A\Phi_{A1}}{r_A}\right] \qquad (1)$$

$$\Phi_A = \Phi_{A1}\left[1 + K_A\Phi_{B1}\Gamma_1\right] \qquad (2)$$

where

$$\Gamma_1 = \left(1 - \frac{K_2}{K_B}\right) + \frac{K_2}{K_B}\left(\frac{1}{(1 - K_B\Phi_{B1})}\right) \qquad (3)$$

$$\Gamma_2 = \left(1 - \frac{K_2}{K_B}\right) + \frac{K_2}{K_B}\left(\frac{1}{(1 - K_B\Phi_{B1})^2}\right) \qquad (4)$$

Where Φ_A and Φ_B denote volume fractions of non-self associated species A (AS-POSS) and self associating species B (phenolic), respectively. Φ_{A1} and Φ_{B1} are the corresponding volume fractions of the isolated AS-POSS and phenolic segments, respectively. r is the ratio of molar volume, V_A/V_B. Self-association equilibrium constants, K_B and K_2, describe the formation of multimers and dimers, respectively. Finally, the K_A is the equilibrium constant describing the association of A with B. In addition, K_B and K_2 are 23.3 and 52.3 at 25℃ of the pure phenolic [11]. In order to calculate the inter-association constants (K_A), the methodology of a least square method has been described in our previous study [12]. Table 3-2 lists all the parameters required by the Painter-Coleman association model to estimate thermodynamic properties for this phenolic/AS-POSS blend. The inter-association equilibrium constant of 26.0 is obtained for the phenolic/AS-POSS blend. However, the K_A=64.6 for the phenolic/PAS blend, implying that the K_A between the hydroxyl group of phenolic and the siloxane group of POSS is equal to 38.6 (64.6-26.0 = 38.6), which is exactly consistent with the previously reported value based on the classical Coggeshall and Saier (C&S) methodology. Therefore, the inter-association equilibrium constant of hydroxyl-siloxane has good correlation between these two methods.

Table 3-2: Summary of the self-association and inter-association equilibrium constants and thermodynamic parameter of phenolic/AS-POSS blends at 25℃

Polymer	V	Mw	Equilibrium Constant		
			K_2	K_B	K_A
Phenolic[1]	84	105	23.3	52.3	
PAS[2]	128.6	162.2			64.6
8-isobutyl POSS[3]	778.6	872.2			38.6
AS-POSS	2058.6	2305.6			26.0

V: Molar Volume (ml/mol), Mw: Molecular Weight (g/mol), K_2: Dimmer self-association equilibrium constant, K_B: Multimer self-association equilibrium constant, K_A: Inter-association equilibrium constant, [1]: reference 11, [2]: reference 12, [3]: reference 11.

3.4 Conclusion

A new nanomaterial based on AS-POSS has been synthesized and the hydrogen bonding interaction of phenolic/AS has been investigated by using FTIR analyses. The inter-association equilibrium constant between the hydroxyl group of the phenolic and the siloxane group of the POSS is determined indirectly from a least square fitting procedure based on the experimental fraction of hydrogen bonded carbonyl group in this blend system. The observed K_A (38.6) of hydroxyl-siloxane is found equal to the value from classical classical Coggeshall and Saier (C&S) methodology.

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Chapter 4. A Novolac type of phenolic nanocomposite from octaphenol-POSS

Abstract

By adding the octaphenol-POSS before the polymerization process (which we called the reaction system) of phenolic resin to join the reaction with phenol and formaldehyde, we can synthesized a series novel novolac type of phenolic/POSS nanocomposite. Each octaphenol-POSS has eight phenol groups, and they can be viewed as eight polymerizable groups in the condensation polymerization process of phenolic resin. In order to demonstrate the occurrence of the reaction, we synthesized another series novolac type of phenolic/POSS nanocomposite by adding the octaphenol-POSS after the polymerization process (which we called the blend system) of phenolic resin for comparison. The thermal properties of these two materials are investigated by DSC, TGA, and the molecular weight distribution of the nanocomposite and dispersion condition of POSS are investigated by MOLDI-TOF and WAXD, respectively.

4.1 Introduction

Despite the emergence of several new classes of thermosets, high performance polymers and several other new generation materials that are superior in some respects, phenolic resins retain industrial and commercial interest, a century after its introduction. Phenolic resins are preferred in a wide range of applications, from commodity and construction materials to high technology aerospace industry. This recognition emerges from the fact that these resins have several desirable characteristics, such as superior mechanical strength, heat resistance and dimensional stability, as well as, high resistance against various solvents, acids and water. They are inherently flame resistant, and evolve low smoke upon incineration. Although phenolics cannot be substituents for epoxies and polyimides in many engineering areas, their composites still find a major market in thermo-structural application in the aerospace industry due to good heat and flame resistance, excellent ablative properties and low cost. These key properties add to their market growth, and as a result of innovative research, new products and applications continue to emerge, demonstrating the versatility and the potential of phenol resins to cope with the ever-changing requirements and challenges of advanced technology. [1-2]

Undisputedly, classical phenolic resins based on resole and novolac dominate the resin market. However, their acceptance as a universal material in many engineering areas is hampered by some of the inherent qualities derived from their special chemical structures. These resins cure at moderately high temperature by a condensation mechanism with the evolution of volatiles, which necessitates application of pressure during molding to form void-free components. The need for the use of catalyst for curing and the limited shelf life of resin at ambient conditions are also major shortcomings of these systems. When compared to many known thermally stable polymers, their thermo-oxidative stability is low. The rigid aromatic units tightly held by the short methylene linkages make the matric brittle. In view of this, a new chemistry is needed to modify the cure of phenolic resins, in particular, a new method is needed to chain extend and/or to cross-link phenolic resins without production of volatiles and allow for extended shelf stability at ambient conditions for the formulated thermosets. In doing so, it is imperative that the modifications do not impair the thermo-mechanical characteristics of the resultant system.

4.1.1 Strategies for designing addition-cure phenolics

Several approaches have been reported for modification of phenolic resins and their cure chemistry. Structural modification to confer addition-cure character has been one thrust area of research [3,4]. Additional-curable phenolic resins with improved thermal and pyrolysis characteristics will be the desirable resins in composites for thermo-structural applications. [5] Higher char-yield leads also to a better heat shielding. Such high char phenolics could be potential candidates as matrices in carbon/carbon composites with obvious advantages [6]. The major strategies in designing addition-cure phenolics are:

(1) Incorporation of thermally stable addition-curable groups on to novolac backbone

(2) Structural modification (transform) involving phenolic hydroxyl groups

(3) Curing of novolac by suitable curatives through addition reactions of OH groups

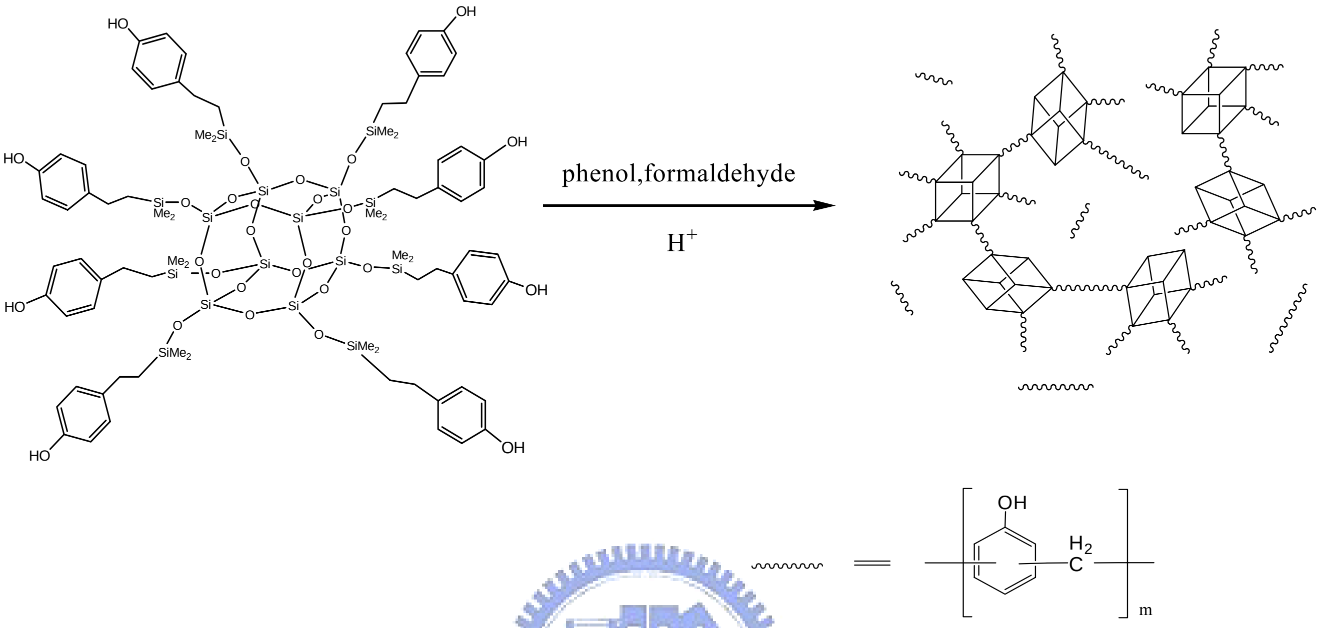
(4) Reactive blending of structurally modified phenolic resin with a functional reactant

4.1.2 Hybrid inorganic/organic crosslinked resins containing polyhedral oligomeric silsesquioxanes

As POSS macromers are incorporated, a kinetic race occurs. The solubility of the POSS in the organic monomer mixture of the resin (phenolics, epoxies, vinyl esters, methacrylics, styrene-divinylbenzene, cyanate esters or dicyclopentadiene) decreases during the cure as the number of monomer molecules (hence the entropy of mixing) decreases. Therefore, phase separation of the POSS macromer may occur sometime during the cure. This would occur in competition with the POSS macromer’s chemical incorporation into the resin. After such phase separation, the POSS macromer may homopolymerize (or copolymerize with smaller amounts of resin monomers) to form POSS-rich phases within the composite as the resin curing continues. This process can compete against random POSS incorporation into the developing resin network. Random incorporation leads to molecularly dispersed POSS monomer units within a homogeneous resin phase. Phase separation will be increasingly favored if the POSS monomer has a low relative reactivity. This will cause monomer drift during the cure which raises POSS concentration relative to the other monomers, favoring phase separation. Anything that increasing the early incorporation of POSS will lower this phase separation. Another type of phase separation process can also operate, even if all the POSS is polymerized randomly into the resin network. POSS macromers bonded into chain segments of the resin may preferentially self-associate with each other, forming POSS aggregates whose structures and sizes are limited by the freedom of motion permitted by the developing resin's chain segmental mobility and the POSS stoichiometry. This process is favored at low crosslink densities where segmental mobility is larger. POSS aggregation has been previously observed in uncrosslinked thermoplastics. Coughlin et al have demonstrated that linear copolymers of ethylene with a mono-alpha-olefin-substituted POSS can form POSS nanocrystalline domains due to self-aggregation of pendant POSS moieties [7]. The extent of such aggregation depends on the mole fraction of POSS present and the method of solidifying the polymer (cooling a melt, precipitation from solution etc.). Such aggregation in crosslinked resin matrices will certainly be dependent on (1) the buildup of crosslinked density as a function of the degree of cure, (2) the relative reactivity ratios of the monomers, (3) the solvent used (if any) and (4) other factors (processing condition etc.).

In this thesis, we used octaphenol-POSS to enhance the thermal properties of phenolic resin, the suitable time of adding POSS and the changes in thermal properties will be discussed.

4.2 Experimental section



Scheme 4-1. Preparation of phenolic/octaphenol-POSS nanocomposite

Synthesis process of phenolic/octaphenol-POSS nanocomposite: reaction system

formaldehyde$_{(aq)}$ (137 g, 37wt%) was placed in a 1000 mL Schlenk flask equipped with a reflux condenser and a mechanical stirrer. Octaphenol-POSS at desired composition was added to phenol solution (188 g), stirred 5 minute, and then added the solution to the flask. Sulfuric acid (10%, 10ml) was added via a syringe. The reaction mixture was then heated to 100℃ under nitrogen and was completed in 22 hours. The solution was washed by hot water (90℃) three times to remove unreacted monomer and extract to remove water layer. The product was dried in a vacuum oven at 180 ℃ for 24 hours. Phenolic/octaphenol-POSS nanocomposite: reaction system can be obtained.

Synthesis process of phenolic/octaphenol-POSS nanocomposite: blend system

formaldehyde$_{(aq)}$ (137 g, 37wt%) and phenol solution (188 g) were placed in a 1000 mL Schlenk flask equipped with a reflux condenser and a mechanical stirrer. Sulfuric acid (10%, 10ml) was added via a syringe. The reaction mixture was then heated to 100℃ under nitrogen and was completed in 22 hours. The solution was washed by hot water (90℃) three times to remove unreacted monomer and extract to remove water layer. The product (pure phenolic resin) was dried in a vacuum oven at 180 ℃ for 24 hours. Dissolve the pure phenolic resin and octaphenol-POSS at desired composition in tetrahydrofuran (THF) and dried in a vacuum oven at 80 ℃ for 24 hours. Phenolic/octaphenol-POSS nanocomposite: blend system can be obtained.

4.3 Characterizations

Differential scanning calorimeter (DSC)

Thermal analysis was performed with a differential scanning calorimeter from DuPont (DSC-9000) with a scan rate of 20 ℃/min and a temperature range of -50~150 ℃. Temperature and energy calibrations were carried out with indium. Approximately 5-10 mg of each blend was weighted and sealed in an aluminium pan. This sample was quickly cooled to -50℃ from the melt for the first scan and then scanned between -50 to 150℃ at 20℃/min. The glass transition temperature is at the midpoint of the specific heat increment.

Wide Angle X-ray Diffraction (WAXD)

XRD spectra was collected on a M18XHF-SPA X-ray diffraction instrument (MacScience Co, Japan), used Co K_α radiation; Bragg's law($\lambda=2d\sin\theta$) was used to compute the spacing.

Thermogravimetric Analysis (TGA)

Thermal stability of the cured sample was investigated by a Du Pont 2050 TGA. The cured sample of 5-10mg was placed in a Pt cell and heated at a heating rate of 10 ℃/min from 30 to 800℃ at a nitrogen flow of 90 mL/min.

MALDI-TOF

All the mass spectra were obtained using a Biflex 3 (Bruker) time-of-flight mass spectrometer. The mass spectrometer was equipped with a 337-nm nitrogen laser, a 1.25-m flight tube, and a sample target having the capacity to load 384 samples simultaneously. The accelerating voltage was set to 19 Kv.

4.4 Results and Discussion

Figure 4-1 displays the DSC thermograms of octaphenol-POSS blended with phenolic (the blend system) as a function of composition, and Figure 4-2 displays the DSC thermograms of the reaction system. For comparison, Table 4-1 shows the summary of T_g of these two figures. The T_g of the blend system decreases with increasing POSS content, while the T_g of the reaction system increases with increasing POSS content (except the 10wt%), which verifies that in reaction system, the octaphenol-POSS joins the polymerization reaction and acts as a crosslinking point to make the thermal properties of the material improve. A T_g depression in the blend system is characteristic of a poor dispersion of POSS, as we mentioned before at Chapter 3, the phenol groups of phenolic resin will form hydrogen bonds with the siloxane groups of the octaphenol-POSS. Apparently, the force of the hydrogen bonds are not strong enough to make the octaphenol-POSS disperse well. For the reaction type, T_g increases with increasing POSS content and then decreases again (10wt%), indicates that octaphenol-POSS joins the polymerization of phenolic and acts as a crosslinking points to make the nanocomposite crosslinke, reduces the free volume and raises the T_g. Figure 4-3 displays the MALDI-TOF of the reaction system phenolic/POSS nanocomposites. The low molecular weight portions (<1500) increase significantly with increasing POSS content, indicates that as the POSS content increases, the steric hindrance of the POSS will lower the reactivity of the phenol groups. In other words, the effect of POSS acts as a crosslinking point competes with the effect of steic hindrance POSS, once the POSS content exceeds a certain degree, the low reactivity will make the thermal property of the material decreases.

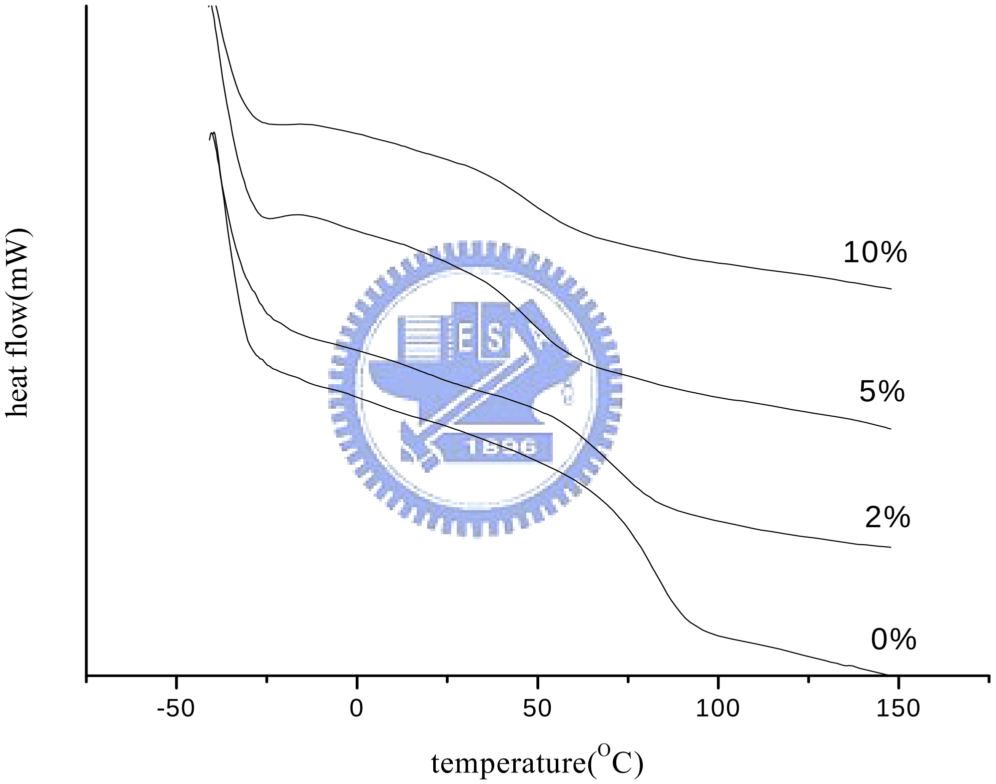


Fig. 4-1 DSC scans of phenolic/octaphenol-POSS (blend system)

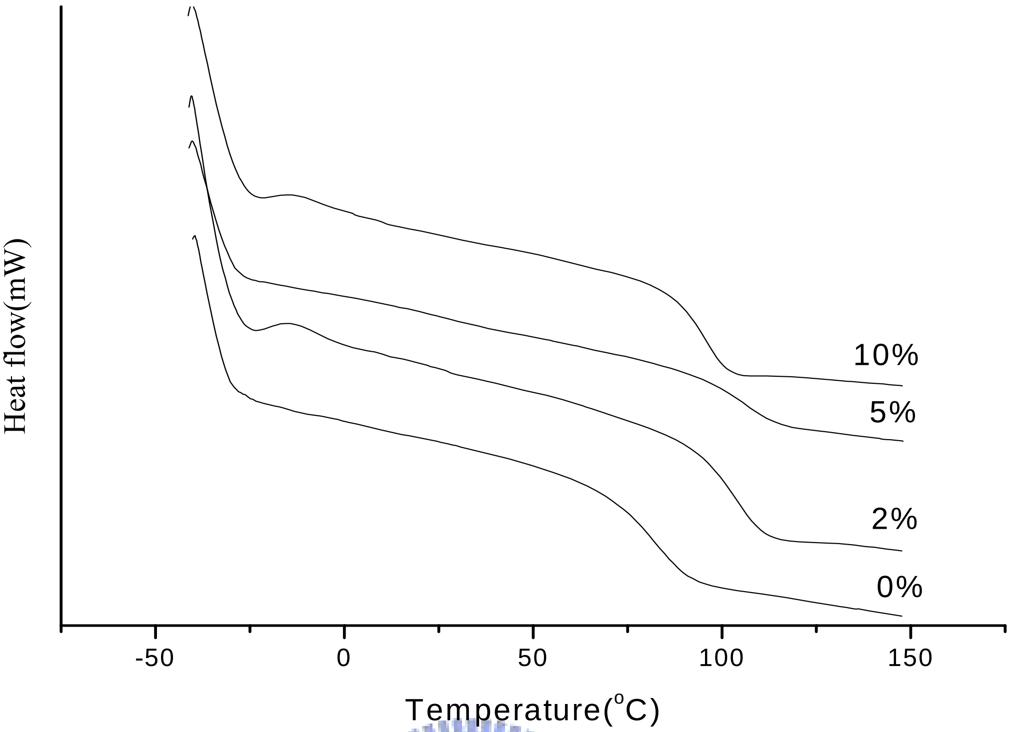


Fig. 4-2 DSC scans of phenolic/octaphenol-POSS (reaction system)

Table 4-1 Comparison of phenolic/octaphenol-POSS for reaction system and blend system(DSC)

TB$_{\mathrm{g\ B}}$of reaction system(℃)	Composition (wt%)	TB$_{\mathrm{g\ B}}$of blend system(℃)
82	0%	82
104	2%	71
106	5%	46
96	10%	47

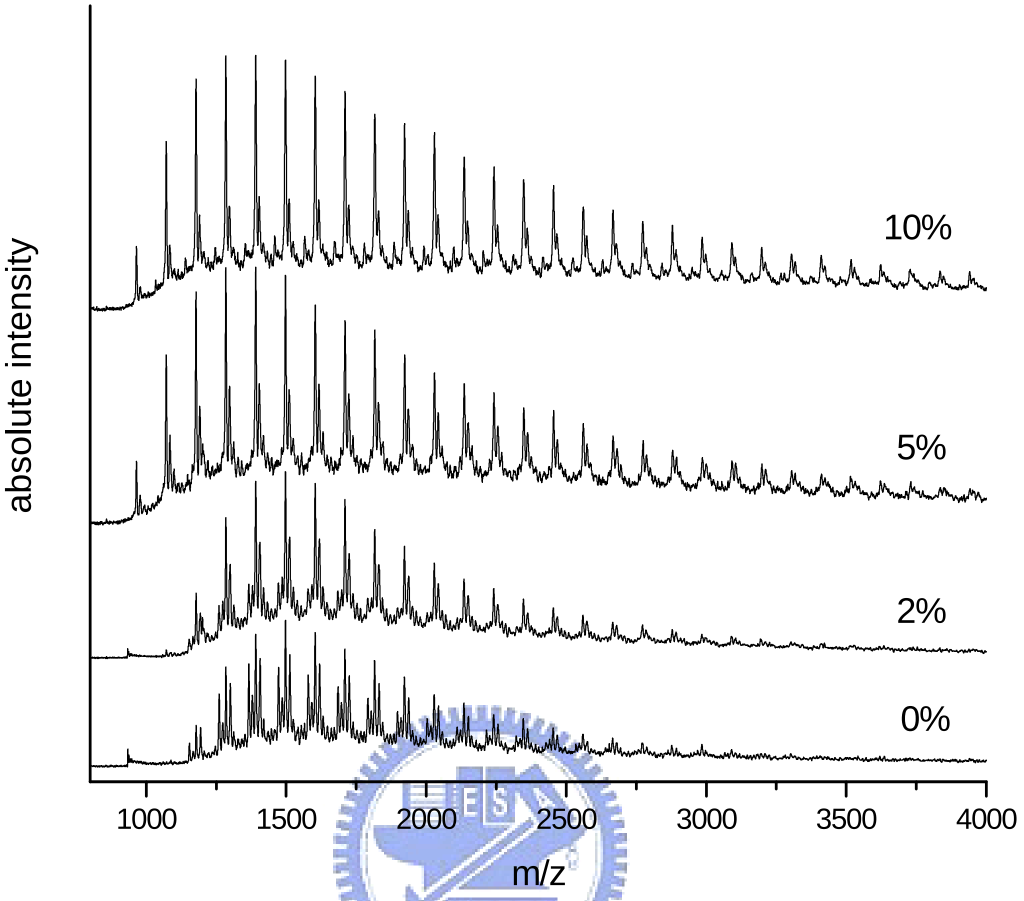


Fig. 4-3 MALDI-TOF of phenolic/octaphenol-POSS (reaction system)

Figure 4-4 and figure 4-5 display the TGA thermograms of the blend system and the reaction system phenolic/POSS nanocomposites, respectively. The decomposition parameters obtained from TGA thermograms are compiled in Table 4-2, including the 5 wt% loss temperatures and char yields. The thermal stability and anaerobic char residue of the blend type decrease with increasing POSS content, while for the reaction type, they increase. The totally different trends between the two types are resulted from the role of octaphenol-POSS play in phenolic: In the reaction system, the POSS joins the polymerization and acts as a crosslinking point, it will definitely increase the thermal stability of the nanocomposite due to the better dispersion of POSS induced by the chemical bond formation. However, in the blend system, the POSS just acts as a nano-filler. Moreover, even at very low POSS loading aggregation appears easily, the poor dispersion will lower the thermal stability.

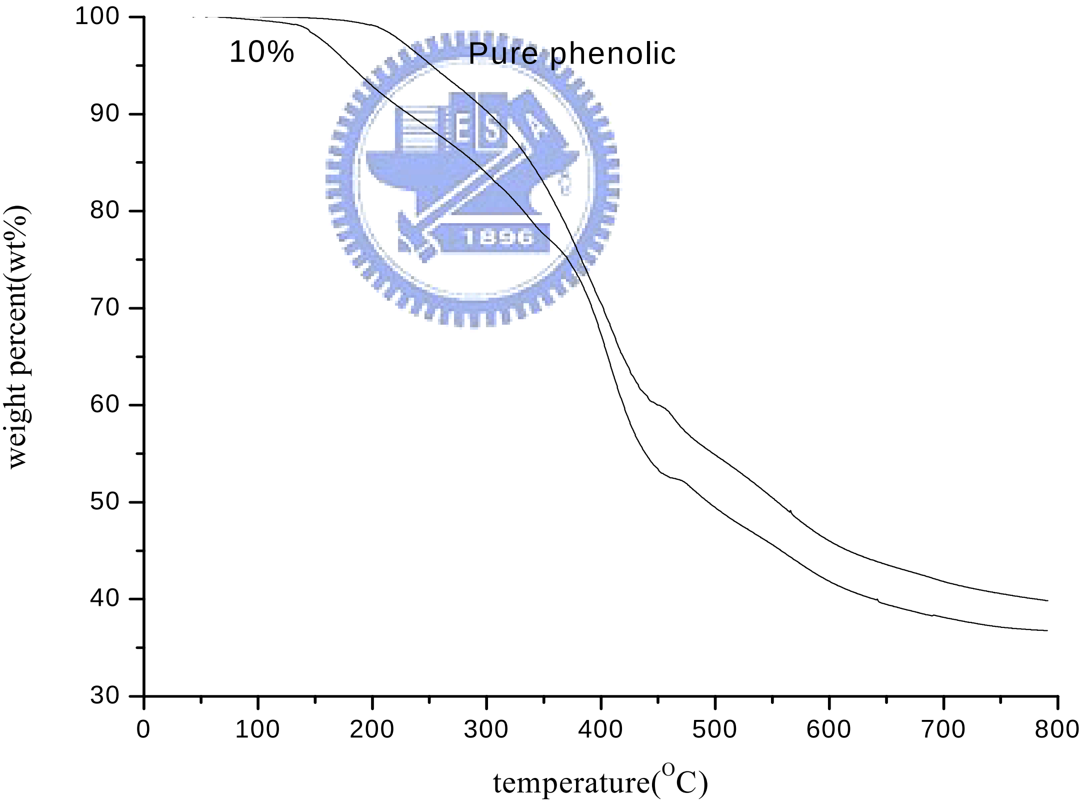


Fig. 4-4 TGA of phenolic/octaphenol-POSS (blend system)

(For clarity, data of 2% and 5% are not shown.)

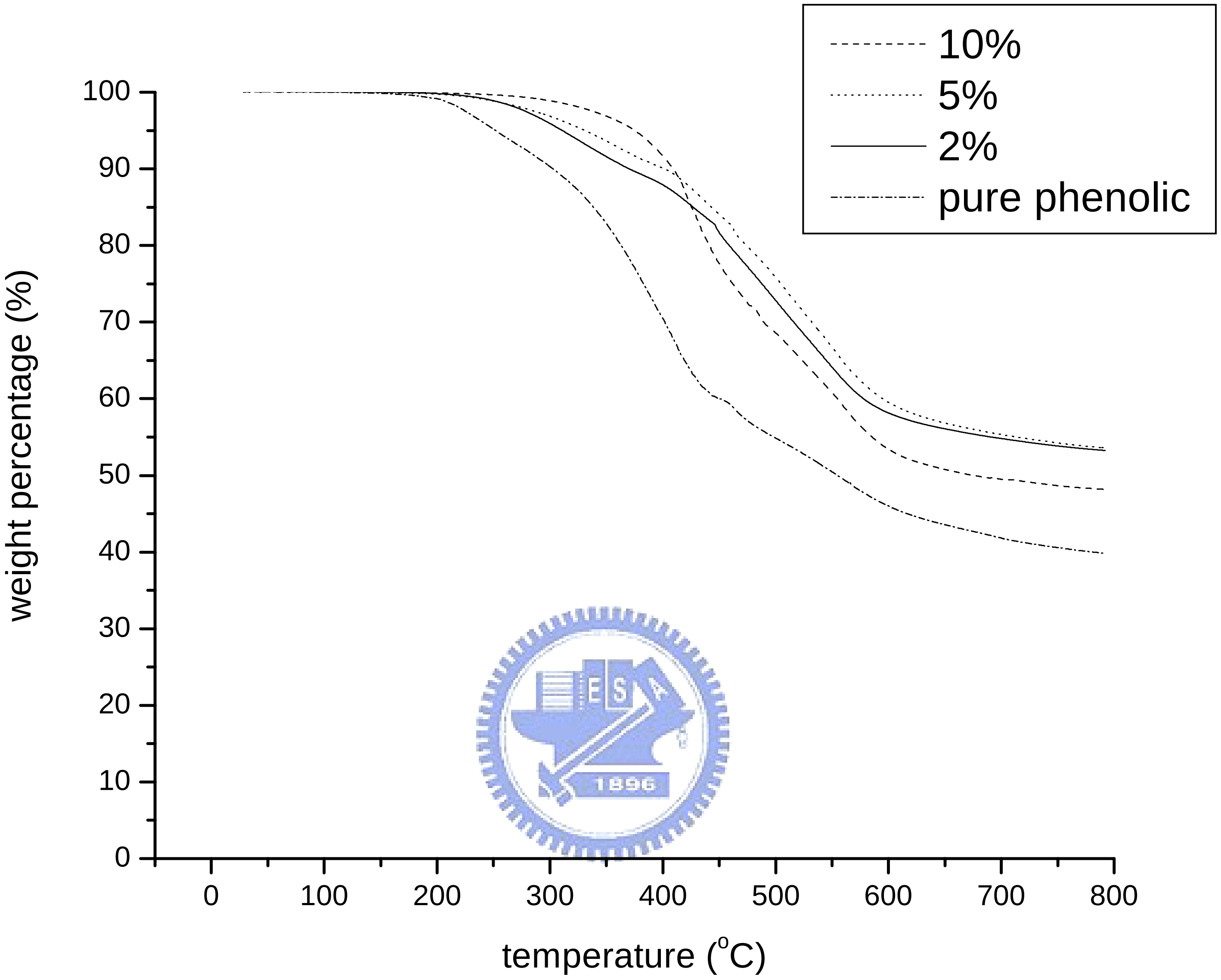


Fig. 4-5 TGA of phenolic/octaphenol-POSS (reaction system)

Table 4-2 Comparison of phenolic/octaphenol-POSS for reaction system and blend system(TGA)

	$TB_{5\%B}$(℃)	char yield(%)
Pure phenolic	251.7	39.8
Reaction system:		
2%	311.3	53.3
5%	330.9	53.6
10%	375.1	48.2
Blend system:		
2%	240.7	41.3
5%	189.8	37.0
10%	180.7	36.8

Figure 4-6 is the WAXD of phenolic/octaphenol-POSS nanocomposite (reaction system). From 0% to 10%, traces of WAXD show only amorphous halo, leading to the conclusion that at reaction system, POSS aggregation is small.

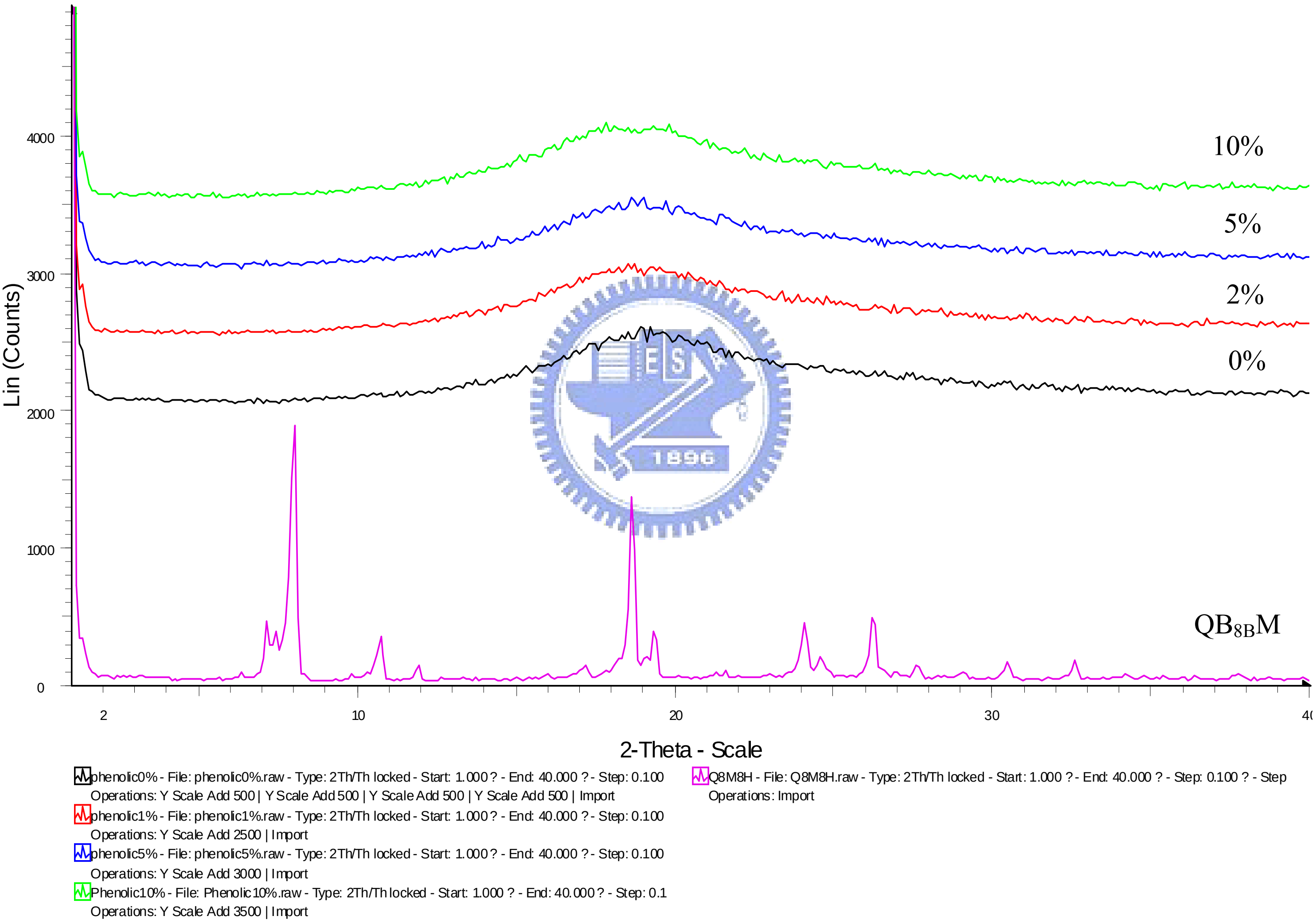


Fig. 4-6 WAXD of phenolic/octaphenol-POSS (reaction system) and Q_8M_8H

4.5 Conclusions

We have successfully synthesized a new novolac type phenolic resin based on the octaphenol-POSS, through carefully choosing the time of adding octaphenol-POSS, the thermal properties will improve dramatically. Compared to the blend system of phenolic and octaphenol-POSS, the thermal properties have totally different trend between the two systems. It can be explained by the poorer dispersion of nano-particles in blend system than reaction system.

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