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Studies on the thermal stability of F- and non-F-containing ladder polyepoxysilsesquioxanes by TGA–FTIR

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Abstract

The thermal stability of non-F- (LPS-I) and F- (LPS-II) containing ladder polyepoxysilsesquioxanes under air and nitrogen was studied by DSC, TGA and TGA–FTIR techniques. The thermally curing temperature for LPS-II is about 20 °C higher than that for LPS-I. Both LPS-I and LPS-II exhibits higher thermal stability under air and nitrogen as observed from TGA, where the decomposition temperatures at 5 and 10% weight loss were above 425 and 480 °C, respectively. Under nitrogen, the higher decomposition temperature and residue from TGA was attributed to the gradual cleavage of C–Si and C–C bonds and high stability of F-containing side-chains (non-broken). Because of the weight gain from the oxidation of silsesquioxanes ($RSiO_{3/2}$) to silica (SiO_2), and gradual cleavage of F-containing side-chains, LPS-II exhibits higher decomposition temperature under air environment than under nitrogen. These phenomena detected from TGA could be observed directly from TGA–FTIR stack plots. As combined techniques for the evolved gas analysis, TGA–FTIR played an important role in explaining the phenomena of degradation related to the change of polymer chain structures during heating. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Ladder polyepoxysilsesquioxanes; Fluorinated; Cleavage; Oxidation; TGA–FTIR

1. Introduction

Since polyphenylsilsesquioxane was first reported as ladder structure in 1960s [1], various ladder polysilsesquioxanes have been synthesized and characterized [2–4]. Compared to the linear structural organopolysiloxanes, these ladder polysilsesquioxanes possess excellent electric and optical properties, high thermal stability and mechanical strength, which could be used as interlayer dielectrics and protective coating films in electronic industry [5,6], membrane separation [7] and other industrial fields [8]. Their unique structure and wide applications have attracted more and more attentions in this area.

Epoxy resin has been widely used in electronic industry as substrates, encapsulants, underfills and sealants, etc., but its thermal and mechanical stability under high temperatures hindered its further applications with the downsize trend of electronic packaging [9]. Therefore, improvement of the thermal stability for the epoxy resin attracts more interests recently [10]. Because of the flexibility and thermal stability, polysiloxane was used to modify epoxy resin in order to improve its thermal and mechanical properties, but the limitation of miscibility between epoxy and polysiloxane restricted this improvement [11]. A reasonable

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consideration is to develop copolymers, which combine the siloxane and epoxy structure together in the same polymer chain, to avoid the limitation of miscibility from blending. As such, both the properties from epoxy and siloxane could be extensively employed.

On the other hand, fluorinated polymers exhibit high thermal stability, chemical inertness, low dielectric constant, and interesting surface properties, etc. [12]. Therefore, such products are widely applied in aerospace, aeronautic and microelectronics, etc., in spite of their high cost. By incorporating the fluorine group in ladder polysilsesquioxanes, some properties of polyepoxysilsesquioxane could be improved further.

As traditional instrument, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and differential thermal analysis (DTA) play important roles in measuring thermal stability of materials. However, by using these measurements directly, it is very difficult to observe the relationship between their thermal degradation and the structure change during heating. The coupling thermal analysis with gas analysis techniques provides a powerful tool in investigating the thermal degradation and its mechanism by which the advantage of each technique is enhanced one after the other. As one of these coupling analyses, TGA–FTIR has been proved to be useful for the study of thermal degradation [13,14]. Particular gas profile or functional group profile exhibits the variation in absorbance intensity over certain spectra region as a function of time or temperature.

Much interest so far in the polysilsesquioxanes has been in the synthesis procedure and structure determination; there are few studies on their thermal properties. In this paper, we focus on the characterization of the thermal stability of ladder polyepoxysilsesquioxanes by means of DSC, TGA and TGA–FTIR. Their thermal degradation in air and nitrogen were evaluated and compared. The explanation for their thermal stability was mainly based on the effect of side-chain groups on the polymer main-chain stability.

2. Experimental

2.1. Materials

The polymers in this study were synthesized by template polymerization method in our laboratory (will report elsewhere), and their corresponding structural scheme were shown in Fig. 1, where LPS-I represents the triblock ladder polyepoxysilsesquioxane with alkyl chain and LPS-II represents its corresponding F-containing counterpart.

2.2. Characterization

TGA, FTIR and TGA–FTIR. The thermogravimetric spectra were recorded on a Perkin-Elmer TGA-7 under air and nitrogen environment at a heating rate of 10 °C/min over a range of 50–850 °C. The TGA outlet was coupled on-line with a Perkin-Elmer FTIR Spectra 2000 spectrometer through a gas cell which was warmed up to 200 °C and stabilized for 2 h before the running of TGA, as a result, the stack plots of TGA–FTIR spectra could be recorded over a range of 200–850 °C. The samples were loaded at around 8.0 ± 0.1 mg.

DSC. The differential scanning calorimetric measurement was performed on a Perkin-Elmer DSC-7 differential scanning calorimeter over a range of 50–350 °C at a heating rate of 10 °C/min under nitrogen environment. The samples were loaded at around 5.0 ± 0.1 mg.

3. Results and discussions

3.1. Differential scanning calorimetry (DSC)

Fig. 2 shows the heat evolution of these ladder triblock polyepoxysilsesquioxanes. The broad peaks indicate the gradual self-curing procedure of epoxy under high temperatures. Because of their similar composition, structure and similar amount of sample loaded, these two polymers showed similar exothermic peak areas during complete curing. However, the temperatures of maximum exothermic effect are different and dependent on the difference of side-chain groups, which may result from the thermal resistance effect of F-group. It is well known that polymers would possess superior resistance to thermal and oxidization after materials are fluorinated. The F-containing group may provide "block effect" for the curing reaction among epihydric groups [12], as a result, the maximum exothermic peak of F-containing polyepoxysilsesquioxane was pushed to higher temperature

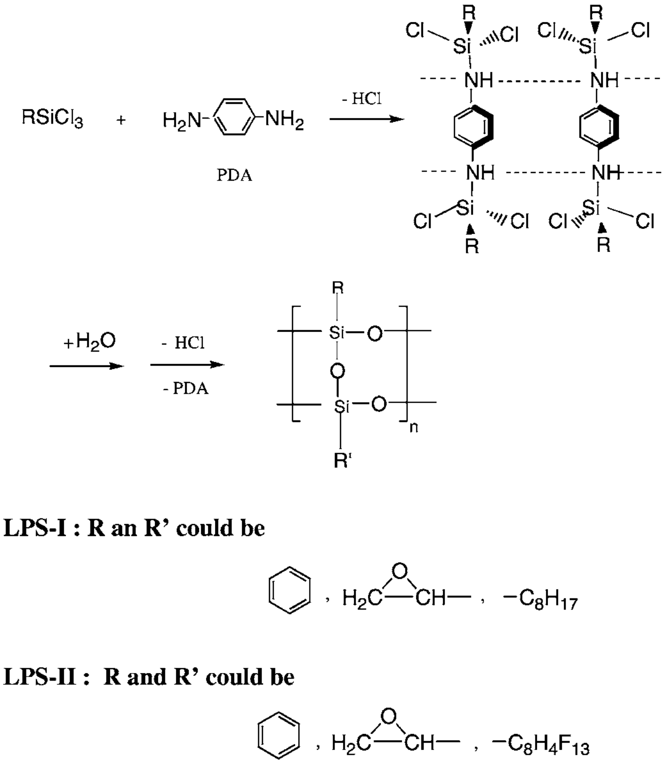


Fig. 1. Schematic outlines of synthesis route of ladder polysilsesquioxanes. LPS-I: ladder phenyl-octyl-ethoxy triblock polysilsesquioxanes; LPS-II: ladder phenyl-F-ethoxy triblock polysilsesquioxanes.

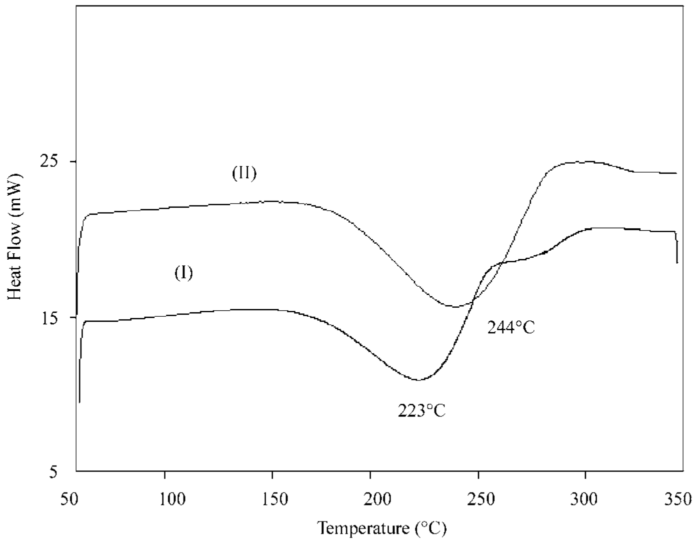


Fig. 2. DSC of LPS-I (I) and LPS-II (II).

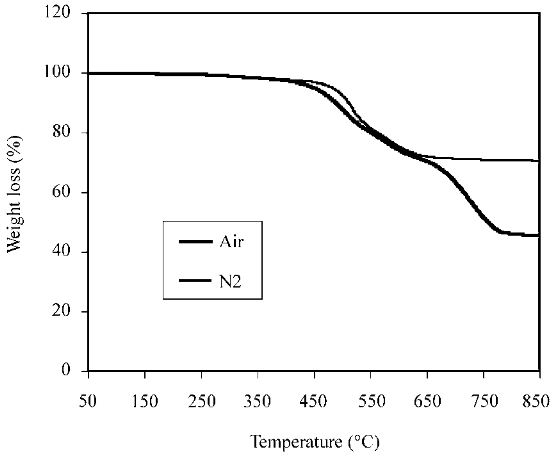


Fig. 3. TGA of LPS-I under nitrogen and air (weighted line).

position. As observed from the width of the peaks, only after cured at 300 °C, both of these two polymers are thermally stable.

3.2. Thermogravimetric analysis (TGA)

The thermal decomposition behaviors under air and nitrogen of these polyepoxysilsesquioxanes (LPS-I and LPS-II) were shown in Figs. 3 and 4, and their decomposition temperatures at weight loss of 5 and 10% were listed in Table 1. Both of these two polyepoxysilsesquioxanes show decomposition temperatures higher than 420 °C under air and nitrogen at which the weight losses are all less than 5%, which demonstrates the superior thermal stability of ladder polysilsesquioxanes [15]. The higher decomposition temperatures of F-containing polysilsesquioxnae (LPS-II) than non-F-containing polysilsesquioxane (LPS-I) under air and nitrogen suggest that the higher thermal stability of polyepoxysilsesquioxanes can also be achieved as expected by incorporating fluorine group in the polymer chains.

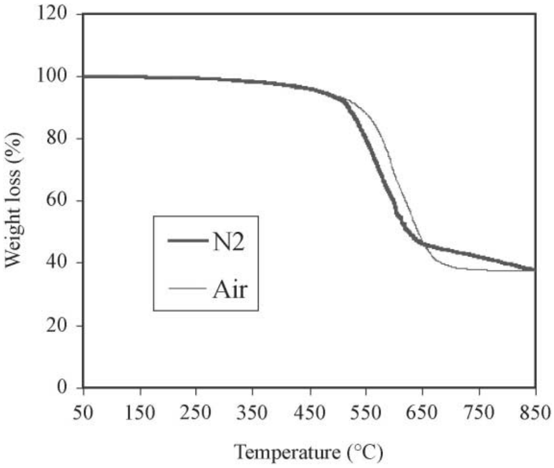


Fig. 4. TGA of LPS-II under nitrogen and air (weighted line).

Table 1
Decomposition temperatures for LPS-I and LPS-II at weight loss of 5 and 10% under nitrogen and air

	LPS-I (°C)		LPS-II (°C)	
	N_2	Air	N_2	Air
5% (weight loss)	471.5	425.1	452.3	482.2
10% (weight loss)	510.3	487.45	482.2	518.8

As shown in Fig. 3, LPS-I is more stable in nitrogen than in air, which is similar as the thermal degradation behaviors of most of other polymers. Under nitrogen, the thermal cleavage of C–Si and C–C bonds result from alkyl chain reaction; and compared to the Si–C_8H_{15} group, the Si–C_6H_5 group is more stable even at higher temperature or just decomposes very slowly, as a result, LPS-I shows one stage decomposition and the residue are higher. Nevertheless, under air, both the thermal cleavage and oxidizing reactions result in the cleavage and oxidation of Si–C_8H_{15} first and then the cleavage and oxidation of Si–C_6H_5, this is why two stage decompositions were clearly observed and the residue are lower.

LPS-II shows different decomposing behaviors from LPS-I under nitrogen and air as shown in Fig. 4. LPS-II shows only one stage decomposition under two environments, but the decomposition temperature in air is higher than in nitrogen. The residue in air were identified as silica by IR and XPS as reported in the literature [15], which means that the ladder main chain would also be oxidized from silsesquioxane ($RSiO_{3/2}$) to silica (SiO_2) under air; and this would result in weight gain in TGA furnace. Because of the higher stability of phenyl and fluorinated side group than that of alkyl chain, the oxidation reaction of main chain from silsesquioxane ($RSiO_{3/2}$) to silica (SiO_2) is faster than the decomposition of side-chain. Therefore, the weight loss from side-chains was compensated by the weight gain from main chain oxidation, and the decomposition temperature was pushed to higher temperature as observed from TGA curve. The similar reason also accounts for the low decomposition temperature and two decomposition stages under air in Fig. 3, where the decomposition and oxidation of alkyl chain is faster than oxidation of $RSiO_{3/2}$ to SiO_2 as well as the cleavage and oxidation of phenyl group.

3.3. TGA–FTIR

The above decomposition phenomena could be observed directly from the stack plot of the coupling TGA and FTIR measurements by analyzing the gas spectra from the thermal decomposition of polymers [13,14]. The X-axis represents the wave numbers of released gas from TGA furnace, Y-axis the intensity of the absorption from the released gas, and Z-axis the temperatures of the TGA furnace.

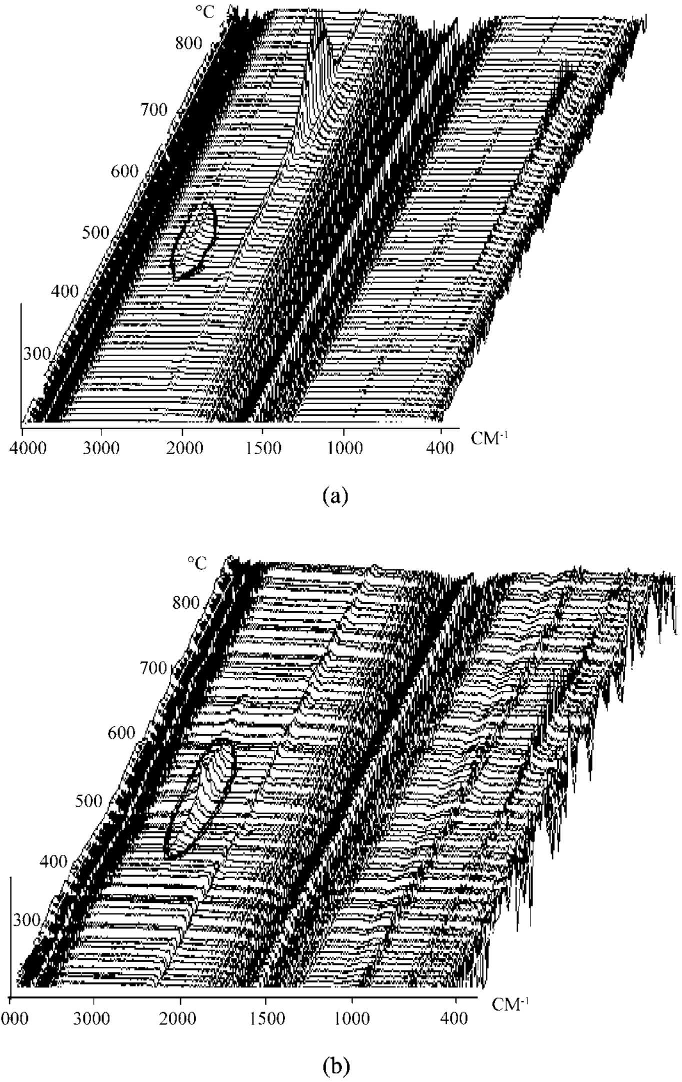


Fig. 5. TGA–FTIR stack plots of LPS-I under air (a) and nitrogen (b).

Fig. 5 shows the stack plot of TGA–FTIR for LPS-I under air (a) and nitrogen (b). In Fig. 5(a), the peak islands (circled) appear at around 2800–3000 cm^{-1} suggest the cleavage of alkyl chain and existence of CH_3– and –CH_2– segments. These peaks started at around 430 °C (425 °C from Table 1). At this temperature, a new hump starting at around 2400 cm^{-1} indicates that large amount of CO_2 was released from the alkyl chain oxidation. The parallel peaks start at almost the same temperature suggested the simultaneous cleavage and oxidation reactions of alkyl chains. The cleavage reaction almost completed at 550 °C while the oxidation is still going on. The abrupt change (maximum hump at 2400 cm^{-1}) of CO_2 volume from 650 to 750 °C suggests the intense oxidation of alkyl chain and phenyl groups. Because of the temperature gaps between 550 and 650 °C, at which represents the lower volume of released gases between two maximums, the TGA curve in Fig. 3 shows two stage decompositions.

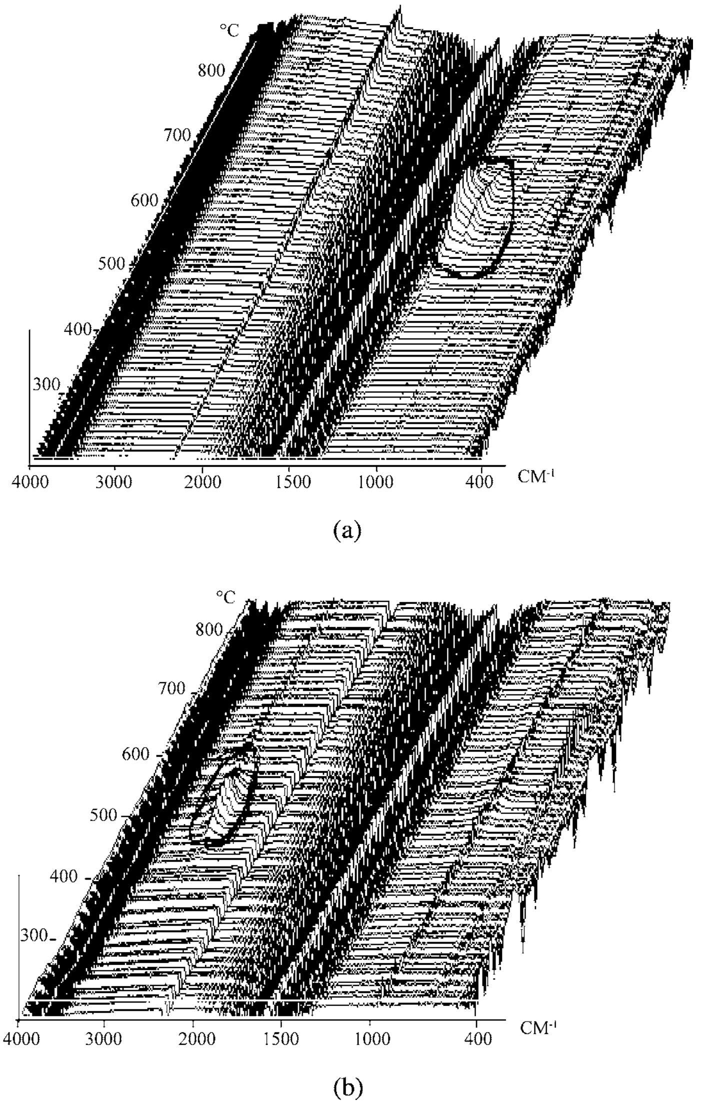


Fig. 6. TGA–FTIR stack plots of LPS-II under air (a) and nitrogen (b).

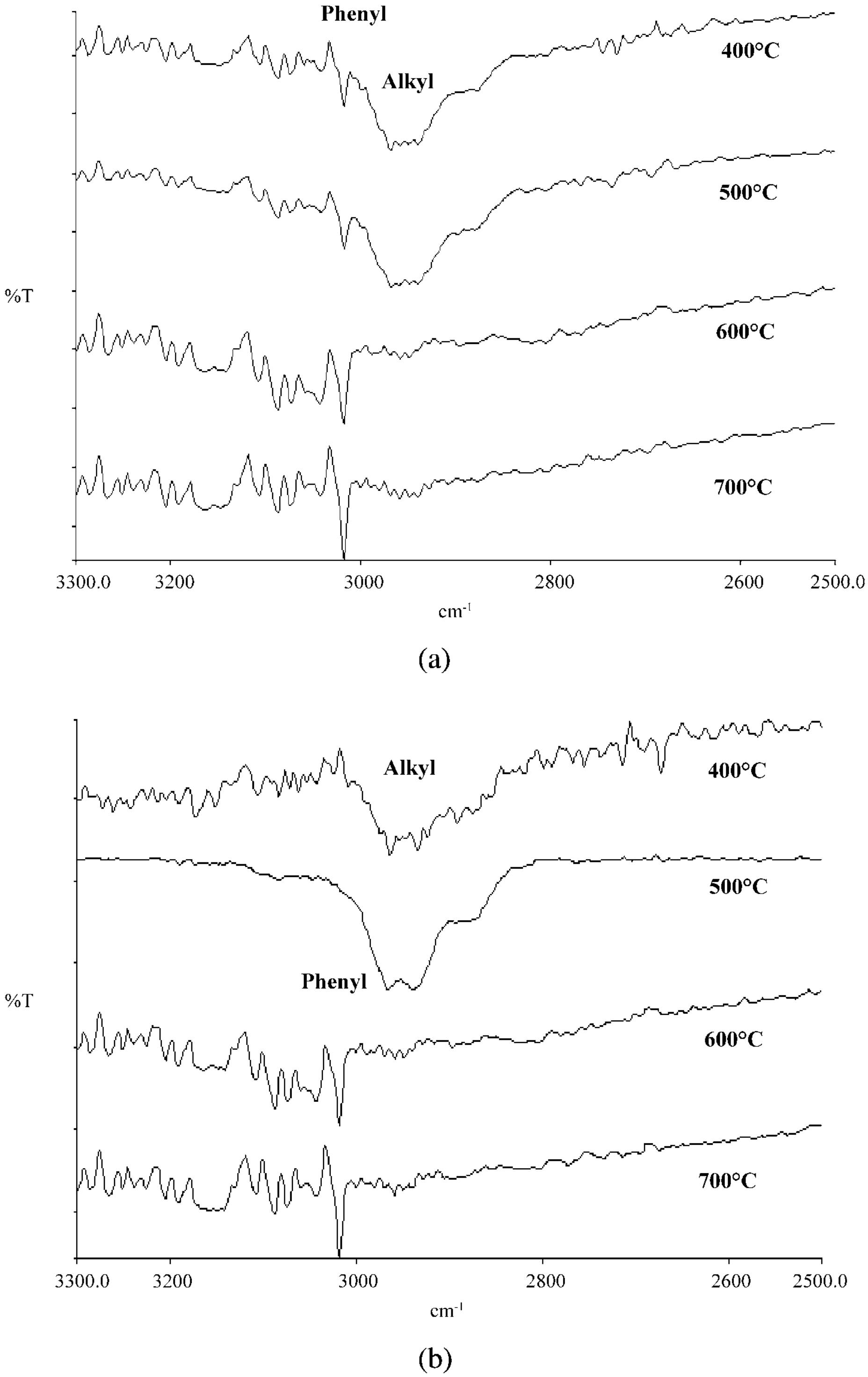
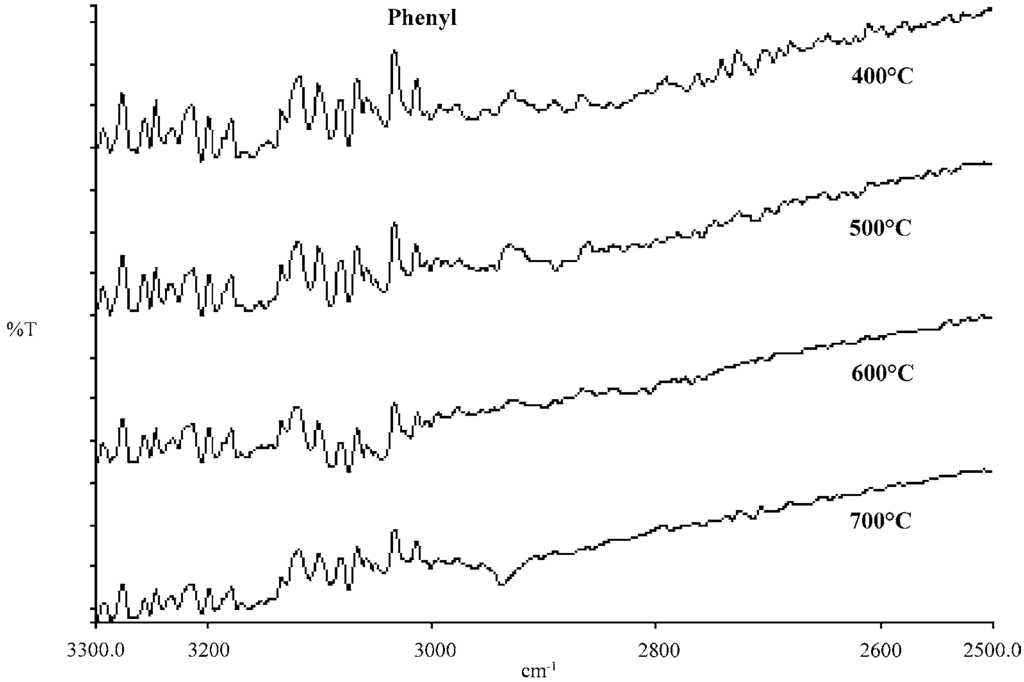
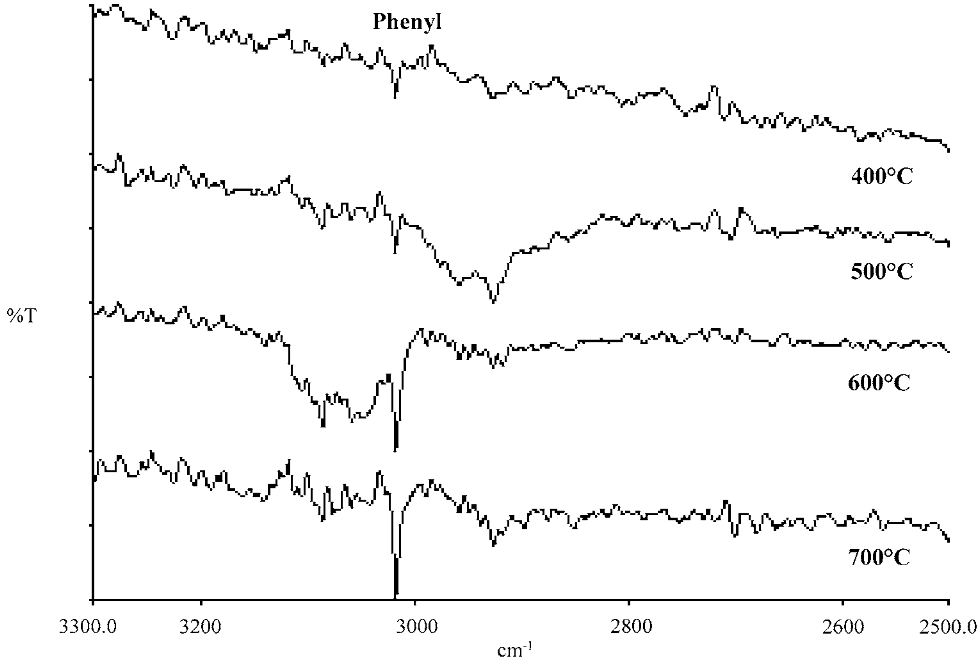


Fig. 7. FTIR spectra of gases evolved with various temperatures: LPS-I under air (a) and nitrogen (b) LPS-II under air (c) and nitrogen (d).



(c)



(d)

Fig. 7. (*Continued*).

From the stack plot of TGA–FTIR for LPS-I under nitrogen in Fig. 5(b), the initial peak islands (circled) appear at around 470 °C, intensify at around 520 °C, then damp to around 630 °C and finally cease at around 680 °C. These changes represent the gradual cleavage of alkyl chains (from 2800 to 3000 cm^{-1}). Apart from these, there are no evident peaks observed. This is what we observed the single stage decomposition in Fig. 3.

As shown in the TGA–FTIR stack plot of LPS-II in air in Fig. 6(a), a new peak island (circled) appeared at around 1200–1350 cm^{-1}, indicates the existence of –CF_2– and –CF_3 segments among the gases detected by IR probe [16]. The less amount of –CH_2– from F-containing side-chain was not detected or oxidized immediately when it was produced. This island started at around 520 °C (518 °C from Table 1) and ended at around 700 °C, which corresponds to the weight loss of TGA curve in Fig. 4. The gradual increase of CO_2 intensity (appeared at around 2400 cm^{-1}) after 550 °C suggests the cleavage and then oxidation of phenyl and alkyl segments from fluorinated side groups, which would also contribute to the weight loss.

However, in the TGA–FTIR stack plot of LPS-II in nitrogen in Fig. 6(b), the accumulation of small alkyl groups was observed around 2800–3000 cm^{-1} (maybe phenyl included). The peak islands (circled) started at 470 °C, ended at 600 °C and then gradually damped with tail till the end of experiment. The fluorinated side-chain is still stable under N_2 even at high temperature because none of F-segments were detected at around 1380 cm^{-1}.

3.4. FTIR

Formation of phenyl radical was considered as the pyrolysis mechanism for polyphenylsilsesquioxanes [17], which should also be observed at around 1600 cm^{-1} on the stack plots of the polyepoxysilsesquioxanes (LPS-I and LPS-II) with phenyl groups [16]. Unfortunately, because of the limitation of the instrument, the absorption bands from 1400 to 2000 cm^{-1} on all the TGA–FTIR plots were not clearly observed at which the absorption of phenyl group appears. Nevertheless, phenyl group should also be detected at around 3050 cm^{-1} [16], which is difficult to be differentiated from the islands representing –CH_3 and –CH_2– groups (around 3000 cm^{-1}) in the stack plots. As a compensation for this, the selected FTIR spectra of gases evolved from these samples at various temperatures were presented in Fig. 7 to show the phenyl cleavage from polymer main chains during heating.

For LPS-I in air (Fig. 7(a)), phenyl even cleavages from around 400 °C and the increase of absorbing intensity (3050 cm^{-1}) with temperatures may be intensified at around 600 °C; the alkyl chains were decomposed and oxidized completely before 550 °C (refer Fig. 5(a)). While in nitrogen (Fig. 7(b)), phenyl is still stable at around 500 °C; the alkyl chains cleavage completely before 600 °C (refer Fig. 5(b)). However, for LPS-II in air (Fig. 7(c)), there is no obvious peaks observed at around 3000 cm^{-1}, while in nitrogen (Fig. 7(d)), large amount of phenyl released were detected at around 550 °C (refer Fig. 6(a) and (b)).

4. Conclusions

The study on thermal degradation of polyepoxysilsesquioxanes by using TGA and the coupled technique TGA–FTIR provides direct observations in understanding and clarifying the decomposition process and related structural alteration during heating treatment. Their stability in nitrogen were mainly determined by the stability of the side-chains, however, their unusual decomposition behaviors under air were attributed to the stability of side-chains as well as the oxidation of polymer main chains from silsesquioxane to silica. By incorporating the F-containing side-chains to the polyepoxysilsesquioxanes, the F-containing side-chains delay the curing process of epoxy group to higher temperature, and improve the thermal stability of polyepoxysilsesquioxanes both under air and nitrogen.

As a consistent collection of gas signals from TGA furnace, the stack plots of TGA–FTIR directly exhibit the group decomposition and oxidation reactions taking place during heating. However, the FTIR spectra of evolved gases with various temperatures provide compensation messages in explaining the peaks overlapped or differentiated with difficulties in stack plots.

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