Thermal Properties and Flame Retardancy of Epoxy Resins Modified with Polysiloxane Containing Epoxy Groups and Redistributed Poly(2,6-dimethyl-1,4-phenylene) Chains

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A B S T R A C T

To improve the thermal property and flame retardancy of epoxy resins, a novel modifier was synthesized through the reaction between the redistributed product of poly(2,6-dimethyl-1,4-phenylene oxide) (REPPO) and the polysiloxane having pendant epoxy groups. Gel permeation chromatography (GPC) was used to confirm the redistribution reaction and identify the average molecular weight of the redistributed products. FTIR and ^{1}H NMR measurements were employed to characterize the structures of the products. This REPPO-containing polysiloxane (PSREPPO) was used to modify a bisphenol A epoxy resin at different contents where 4,4'-diaminodiphenyl-methane (DDM) acting as the curing agent. The cured samples were examined by scanning electron microscope (SEM), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and limited oxygen-index (LOI) methods. The SEM results showed that the use of PSREPPO has improved the phase compatibility and increased toughness of the samples. The DSC results showed that the modifier could improve the T_gs of the epoxy resins. An epoxy/PSREPPO ratio of 100/40 gives an increase of 26.53ºC in its T_g value compared to the unmodified epoxy resin. The TGA results showed that the $T_{d50\%}$ of the samples increased also with the increase of PSREPPO content; although it decreased when the content of PSREPPO exceeded above a certain value. Char yield at 700ºC and LOI values increased with the increase of the content of PSREPPO. In conclusion, the PSREPPO-modified samples improved the thermal properties and flame retardancy of the epoxy resins.

INTRODUCTION

Epoxy resins, one of the most important classes of materials in chemical engineering, have been widely used in many fields, such as protective coatings, adhesives, and microelectronic packagings. With the development of new technologies, higher standards for materials are required and the heat resistance and flame retardancy of the present epoxy resins cannot meet the requirements of these applications [1]. Therefore, the epoxy resins must be modified to meet the criteria of these applications.

Much work has been done to improve the flame retardancy of epoxy resins and a great progress has been achieved so far. At present, with the consideration of avoiding the generation of toxic and halogenated gases, the trend is toward using environment-friendly flame retardants to modify the

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epoxy resins. One example is the use of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), a versatile thermoplastic material with high heat resistance and flame retardancy, which is considered as a choice and has been used to modify the epoxy resins [2]. But as a nonpolar thermoplastic material with high molecular weight, it is immiscible with epoxy resins. Phase separation occurs in the blending of the two materials [3,4]. According to previous reports, it can undergo a redistribution reaction [5-7] in the presence of certain catalyst and phenol(s), giving low molecule weight products. The redistributed product of poly (2,6-dimethyl-1,4-phenylene oxide) (REPPO) with low molecular weight might show better miscibility with the epoxy resins. But, when it is used to modify the epoxy resin, the thermal property of the samples is impaired with the increasing content of REPPO [8].

The reason for this might be that some of the epoxy groups of the resin are consumed by hydroxyl groups of REPPO. One possible solution may be the use of polysiloxanes with pendant epoxy groups which can compensate for the consumed epoxy groups and improve the flame retardancy since it is non-flammable. As far as we know, no one has studied the combination of REPPO and polysiloxane with pendant epoxy groups to improve the thermal property and flame retardancy of epoxy resins.

In this work we synthesized a novel modifier containing REPPO chains with pendant epoxy groups through the reaction between REPPO and the polysiloxane having such pendant epoxy groups. REPPO was obtained through the redistribution reaction of PPO and was confirmed by the GPC and FTIR analysis. The structure of REPPO-containing polysiloxane (PSREPPO) was confirmed by FTIR and ^{1}H NMR analysis, as well. This novel modifier was used at

different contents to modify the epoxy resin with DDM as a curing agent. The glass transition temperature (T_g) values, thermal stability, and flame retardancy of the cured products were characterized by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) and determination of limited oxygen index (LOI).

EXPERIMENTAL

Materials
Bisphenol-A epoxy resin, (Ep828 with an epoxide equivalent weight of 196 g/eq) was purchased from Shell Chemical Co. (Houston, USA), poly (2,6-dimethyl-1,4-phenylene oxide) from Asahi Kasei Co. (Tokyo, Japan), and bisphenol A (BPA) from Wuxi Resin Factory of Bluestar New Chemical Materials Co. Ltd. (Wuxi, China). Benzoyl peroxide (BPO) was purchased from Nanjing Silicon Chemical Co. Ltd. (Nanjing, China), allyl glycidyl ether (AGE) and methylhydrosiloxane-dimethylsiloxane copolymer (MHS-DMS copolymer) from Xinghuo Chemical Co. (Yongxiu, China), and triphenyl phosphine (TPP) from Aldrich (Saint Louis, USA). 4,4′-Diamino-diphenyl-methane (DDM) was purchased from ShangHai SSS Reagent Co. Ltd. (Shanghai, China). All solvents were either reagent grades or purified by standard methods.

Synthesis
Samples were prepared through three major procedures: the redistribution of poly(2,6-dimethyl-1,4-phenylene oxide), the synthesis of ES, and the reaction between REPPO and ES.

The redistribution reaction, shown in Scheme I,
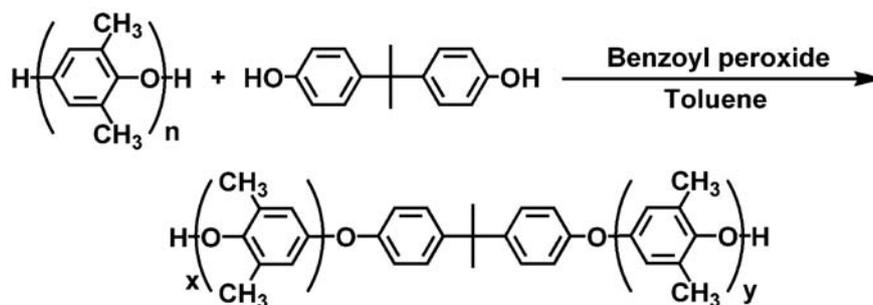
Scheme I. The redistribution reaction of PPO.

was carried out in a four-necked flask equipped with a stirrer, a refluxing condenser, an inert gas inlet and a dropping funnel to which 30 g PPO, 5 g bisphenol A and 100 mL toluene were added. The flask was heated to 85ºC and stirred until the PPO was completely dissolved in toluene. BPO (2 g) was dissolved in toluene and added dropwise through the dropping funnel into the flask. The reaction kept running for 5 h while N_2 was charged into the flask during the whole process. When the reaction was over, the REPPO was precipitated and filtered by adding methanol into the solution and washed by methanol several times.

As it is shown in Scheme II, the synthesis of PSREPPO is consisted of two steps. In the first step, involving the preparation of ES, was according to our previous reports [9,10]. Subsequently, to a three-necked flask equipped with a stirrer, a refluxing condenser, an inert gas inlet, and a dropping funnel were added 10 g REPPO and 2 g ES dissolved in 40 g toluene. The flask was heated to 120ºC, and 20 g toluene solution containing 0.3 g TPP was added to the flask dropwise through the dropping funnel. The reaction went on for 8 h and then the solvent was removed using a rotary evaporator to obtain the PSREPPO.

Curing Reactions of the Epoxy Resins
The samples were obtained by curing the epoxy resins with the PSREPPO prepared above. The epoxy resin, 0.2 wt% TPP and the PSREPPO were mixed together and heated to 100ºC for 30 min, followed by the addition of DDM and stirring until it was dissolved completely. The samples were obtained after the mixture was cured at 90ºC for 2 h, 150ºC for 2 h, 200ºC for 2 h, and 220ºC for 1 h in vacuum, respectively. To illustrate the effect of PSREPPO, unmodified epoxy resin sample was also prepared under the same curing conditions.

Methods of Testing
Gel permeation chromatography (GPC) measurements were performed on a Waters 515-410 gel permeation chromatograph (515-410, Waters, USA). The
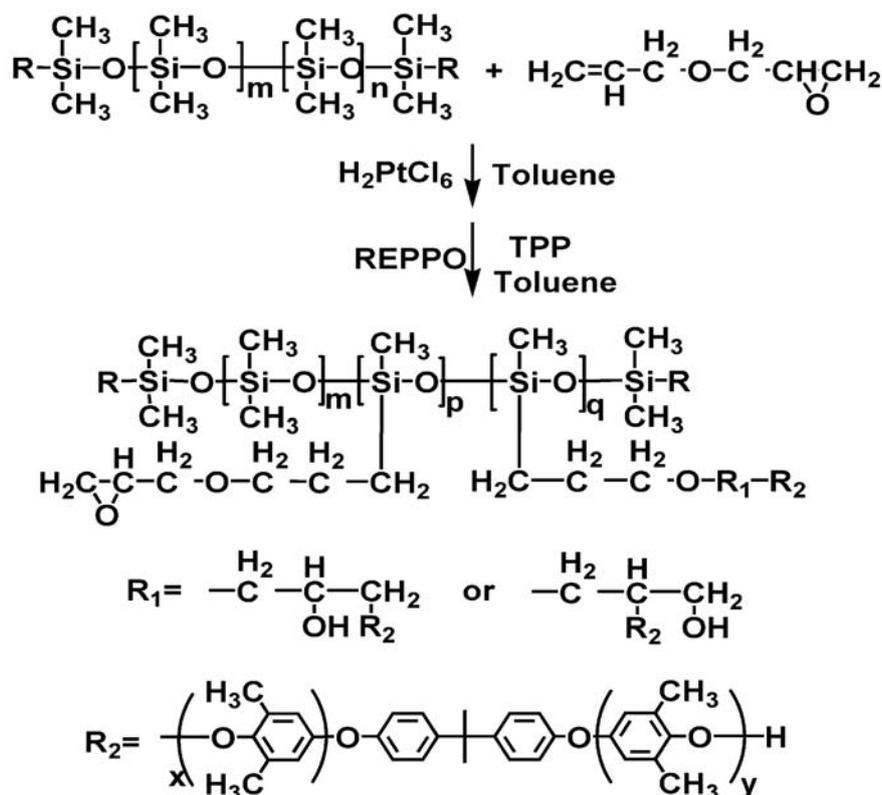
Scheme II. The synthesis of the PSREPPO.

chemical structure of PSREPPO was characterized by FTIR and ^{1}H NMR techniques. The FTIR spectrum was recorded with Fourier transform infrared spectroscopy (RFX-65A, Analect, USA). ^{1}H NMR was performed using a 400 MHz NMR spectrometer (DRX-400, Brüker, Germany) and CDCl$_3$ as a solvent. Scanning electron microscopy (SEM) was performed with a Philips XL-30 microscope (Netherlands). The samples were coated with gold to obtain SEM micrographs. DSC measurements were performed on all samples by a differential scanning calorimeter (DSC-7, Perkin-Elmer, USA) in nitrogen atmosphere, at a heating rate of 20ºC/min. The thermogravimetric analysis (TGA) was performed by a thermal analyzer (Pyris-1 series, Perkin-Elmer, USA) at a heating rate of 20ºC/min in both air and nitrogen atmosphere. The LOI values were measured using a ZRY-type instrument (Nanjing Jiangning Analytic Instrumental Factory, China) with a test specimen bar of 120×6×3 mm according to the standard "oxygen index" test ASTM D2863-77.

RESULTS AND DISCUSSION

Synthesis and Characterization of REPPO
The GPC curve of the redistributed products of PPO is shown in Figure 1. It can easily be seen that there exist two kinds of products having average molecular
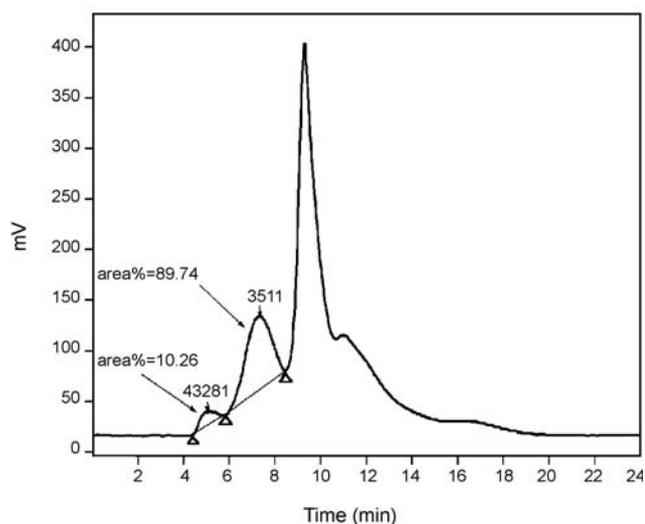

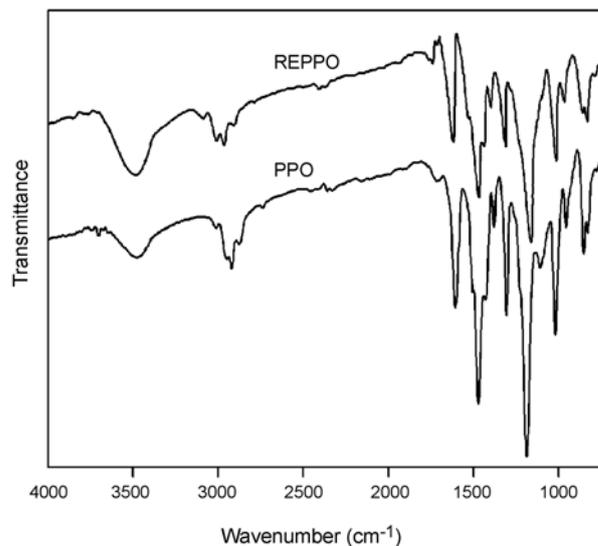**Figure 1.** The GPC curves of the redistributed PPO product.

Figure 2. FTIR spectra of PPO and REPPO.

weights of 43281 and 3511, respectively. The reason for this is probably due to the presence of Mannich base type end groups with lower reactivity than normal phenolic end groups [6] in PPO. When PPO underwent redistribution, the molecules containing Mannich base type end groups did not redistribute. It can be easily seen from the GPC curve that most of the PPO molecules are redistributed. An amount of 89.74% of all the redistribution products has an average molecular weight of 3511, which proves the recurrence and extent of redistribution reactions.

FTIR Analysis
As can be seen from the FTIR spectra of PPO and REPPO in Figure 2, both show the characteristic absorption peaks at 1020 cm^{-1} and 1185 cm^{-1} (phenylene ether) and 1606 cm^{-1} (aromatic ring). The major difference between them is the intensified absorption peak of REPPO at 3400 cm^{-1} (-OH), which indicates the increase in the amount of –OH groups being achieved. This increase of –OH groups also proves the occurrence of the redistribution reaction.

Figure 3 shows the FTIR spectrum of ES and PSREPPO. As can be seen from Figure 3, the absorption peak of PSREPPO at 908 cm^{-1} (epoxide group) has been decreased and its absorption peak at 3400 cm^{-1} is intensified compared to the corresponding absorption peaks of ES, indicating the consumption of epoxide groups and the increase of –OH groups
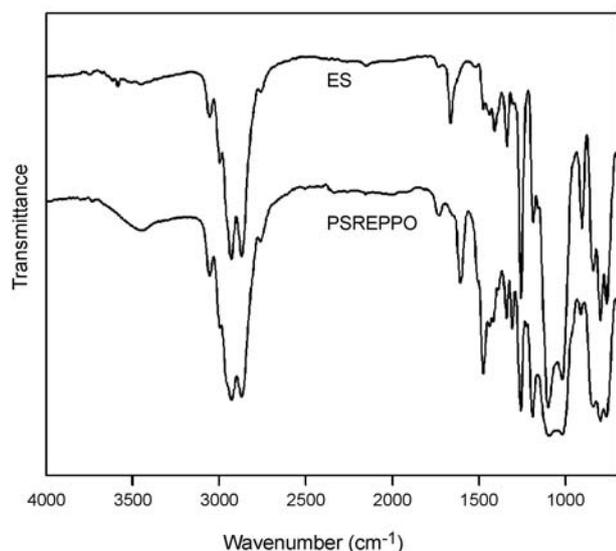
Figure 3. FTIR spectra of ES and PSREPPO.

which demonstrates the occurrence of the reaction between REPPO and ES.

^{1}H NMR Analysis

The structure of PSREPPO was further confirmed with ^{1}H NMR (Figure 4). The reaction between –OH and epoxide group might lead to the formation of two kinds of groups (i.e., –CH$_2$-CH (OH)-CH$_2$-R$_2$ and –CH$_2$-CH(R$_2$)- CH$_2$OH) by means of α and β additions. Both groups are observed in the ^{1}H NMR spectrum of PSREPPO. The peaks at δ = 2.01-2.14 ppm are attributed to the above two groups, and demonstrate the occurrence of the reaction of the -OH and epoxide ring.

SEM Analysis of the Cured Epoxy Resins

To illustrate the effect of PSREPPO, SEM micropho-tographs were obtained, which are shown in Figures 5a and 5b. It may be easily noticed that both samples contained dispersed particles immiscible with the epoxy phase. However, a lower population of the immiscible particles is observed in the sample modi-fied with PSREPPO (Figure 5b). This population decrease implies that PSREPPO rather than REPPO shows better miscibility with the epoxy resins. The epoxy groups in PSREPPO contributes to the improve-ment of the miscibility of PSREPPO and the epoxy resin. When the epoxy resin is cured, these epoxy groups can react with DDM more easily than the phe-nol groups in REPPO and readily enter into the cross-link network of epoxy resins, which further improves the miscibility of PSREPPO and epoxy resin.
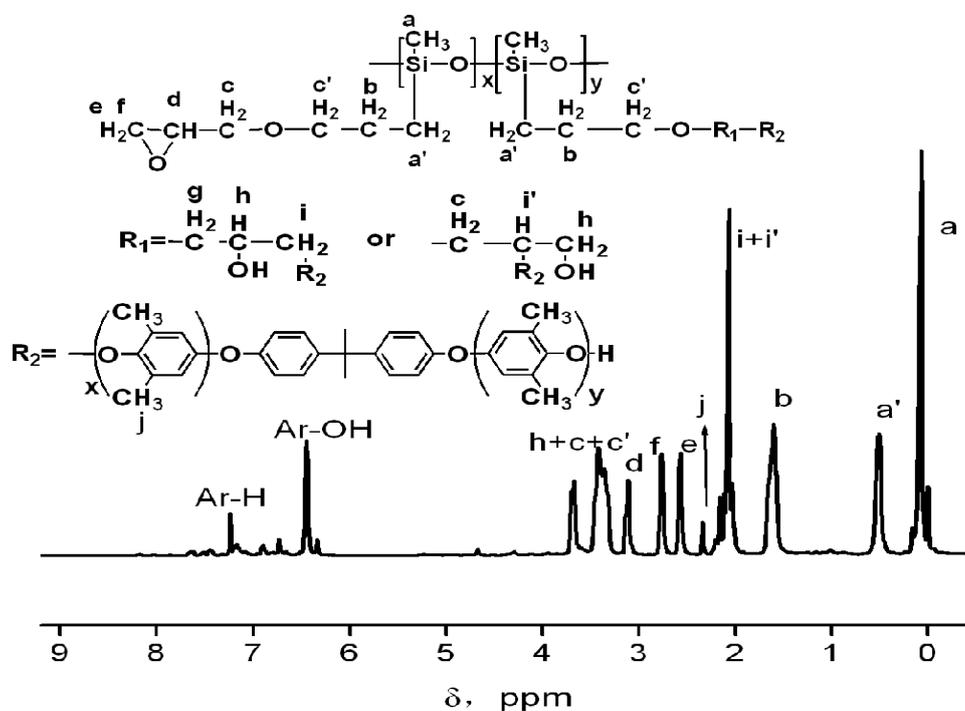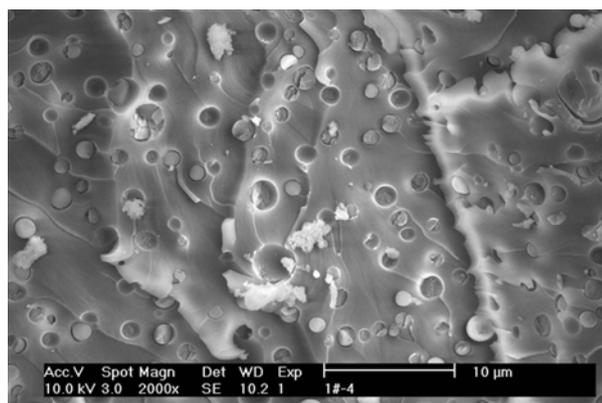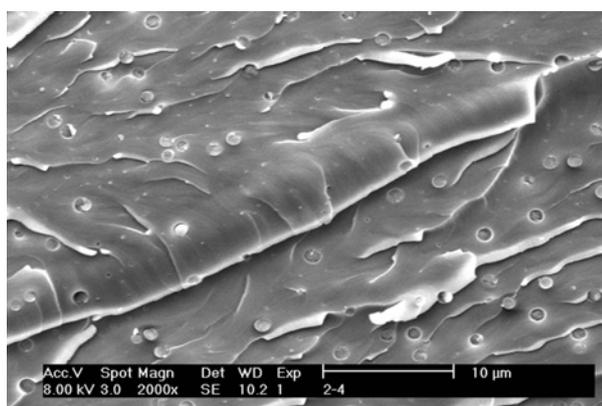

Figure 4. ^{1}H NMR spectrum of PSREPPO.

(a)

(b)

Figure 5. SEM micrographs of samples modified with: (a) REPPO (40 wt%) and (b) PSREPPO (40 wt%).

It can also be observed from Figures 5a and 5b that both the fracture surfaces had the river markings, although the systematic increase in the number of river markings and the corresponding surface roughness could be observed in PSREPPO-modified sample. This increase indicates that the PSREPPO-modified sample has a better toughness property
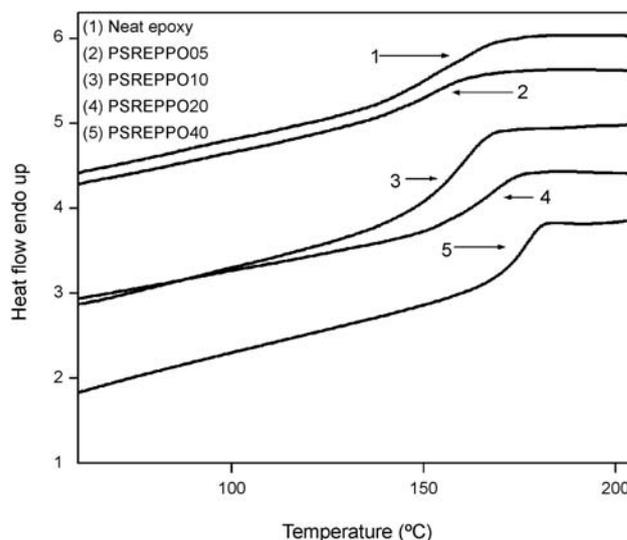

Figure 6. DSC curves of the cured epoxy resins.

compared to the REPPO modified sample.

DSC Analysis of Cured Epoxy Resins

The T_gs of the cured samples were obtained by DSC measurements, and the results are shown in Figure 6 and Table 1. It may be observed that the T_gs of the cured samples have increased with the PSREPPO content. The reason for the increase in T_gs of the cured samples is probably due to the bulky rigid REPPO part of the PSREPPO molecules hindering the free movement of the chains in the cured system. Another reason for this increase of T_gs could be due to increase in cross-link density of the cured system. The polysiloxane has provided extra epoxide groups that would compensate those consumed by the reactions between REPPO and the epoxy resins, leading to higher cross-link density of the cured systems.

Table 1. Summarized data on the properties of the PSREPPO-modified epoxy resin.

Composition	T_g (ºC)	$T_{d50\%}$ (ºC)		Char yield at 700ºC (wt%)		LOI
		N_2	Air	N_2	Air	
Ep/DDM=100/26.7	150.85	433.11	448.23	20.6	0.8	19.8
Ep/PSREPPO/DDM=100/5/26.7	152.80	432.68	489.33	22.6	5.2	22.0
Ep/PSREPPO/DDM=100/10/26.7	161.25	473.17	509.38	24.9	6.9	22.5
Ep/PSREPPO/DDM=100/20/26.7	167.86	483.78	567.99	28.4	19.0	24.6
Ep/PSREPPO/DDM=100/40/26.7	177.38	460.21	566.83	32.4	24.9	26.3

TGA Analysis and Flame Retardancy Analysis

TGA analysis is another powerful method to illustrate the degradation of the testing samples by recording the quality changes of the samples with temperatures. The temperature for 50% weight loss of the samples is a useful index that well reflects the heat-degradation resistance of the samples. As it is presented in Table 1 and Figures 7a and 7b, the $T_{d50\%}$ of the testing samples improves greatly when PSREPPO is added, for the addition of the PSREPPO increases the heat-degradation resistance of the cured resin. The reason is that silicon-contained polysiloxane segment is very flexible and can easily dissipate heat. When it is incorporated into the system, more heat dissipation can be achieved. Thus, an extra amount of energy to offset this heat dissipation will be needed to achieve increased thermal stability.

The reduction in $T_{d50\%}$ is very small when PSREPPO/Ep ratio is 5%, where it may be regarded the same as the unmodified epoxy resin. This shows that the addition of 5% PSREPPO is not enough to change the $T_{d50\%}$ of the epoxy resin significantly. With the increase in PSREPPO content the $T_{d50\%}$ increases significantly as well. But, as the PSREPPO/Ep ratio has been raised to 40%, the $T_{d50\%}$ has dropped in comparison to that of the samples with a PSREPPO/Ep ratio of 20%. This decrease can be attributed to the fact that when PSREPPO content exceeds a certain value, despite being chemically bonded into the network, the PSREPPO chains do not disperse well in the continuous epoxy resin matrix due to their polarity differences. In some areas, phase separation has occurred. Thus, when subjected to high temperatures, degradation occurs first in areas that contains higher amount of epoxy, which results in samples with lower $T_{d50\%}$ values.

The char yields at 700°C shown to be increased both in N_2 and air, especially in air, when PSREPPO is introduced into the system. Such increase has been reported as an implication of improvement in flame retardancy [11,12], which has also been testified by the limited oxygen index analysis. It can be easily noticed that when PSREPPO is incorporated into the epoxy compositions, the LOI is raised from 22 to about 25, which is an indication of increased flame retardancy.
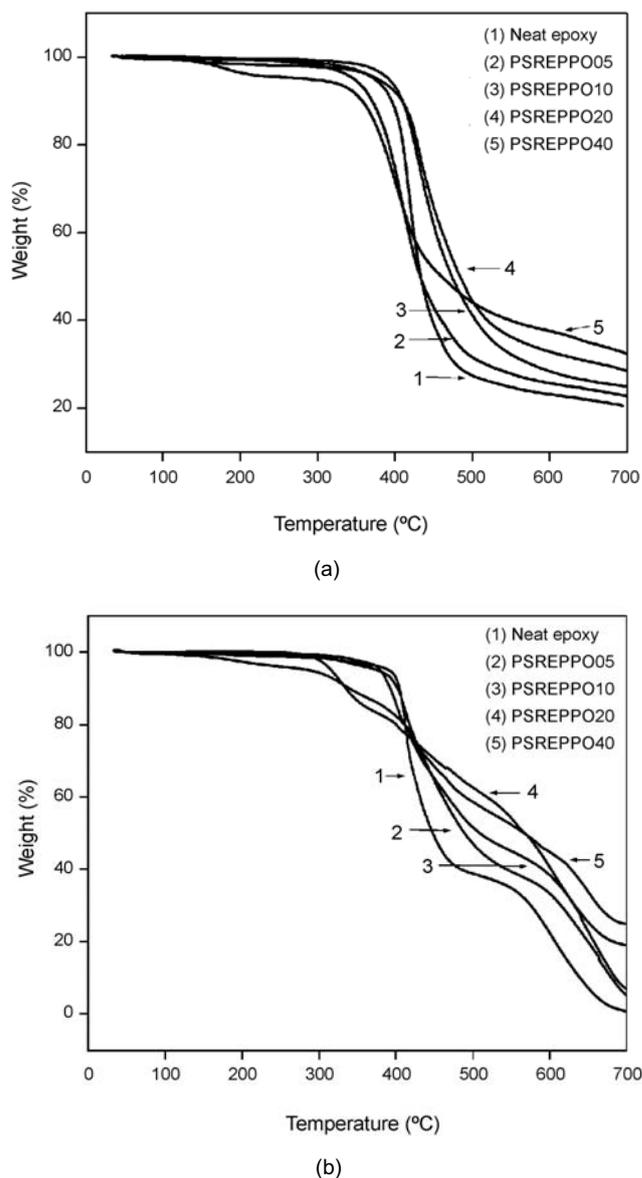
Both the polysiloxane and the REPPO have

(a)

(b)

Figure 7. TGA analysis curves of the cured samples: (a) in N_2 and (b) in air.

contributed to the improvement of the char yields and LOI. First, the existence of Si, which is hard to vaporize even at elevated temperature, is rather critical for the higher char formation of the system. When the samples are subjected to combustion, an inorganic heat-insulation layer containing the –Si-O-, -Si-C- bonds are formed. The REPPO portion of PSREPPO might form a protective layer due to its aromatic structure. The layers act as a barrier that not only prevents the overflow of the combustion product but also inhibits the further heat-pyrolysis of the polymer. Thus, the PSREPPO incorporated samples possess

higher LOI values than the samples without any PSREPPO.

CONCLUSION

In this paper, PSREPPO was synthesized to improve the property of the epoxy resins. GPC, FTIR and ^{1}H NMR techniques were used to confirm the occurrence of reaction and the structure of the products. DSC measurements showed that the T_g of the modified epoxy resins increased with the increase in PSREPPO content. TGA analysis and LOI values demonstrated the improvement in heat-degradation resistance and flame retardancy of the cured samples. Consequently, the use of PSREPPO to modify the epoxy resin improved the thermal stability and flame retardancy of the cured epoxy resins which would make it more useful for more demanding applications.

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