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Synthesis of a novel phosphorus-containing polysiloxane and its use as the modifier of thermal properties of an epoxy resin

Summary — A novel epoxy resin modifier, phosphorus-containing epoxide siloxane (PES) with pendant epoxide and cyclic phosphorus groups in the side chains of the polysiloxane backbone, was synthesized *via* the ring-opening reaction of epoxy siloxane (ES) with 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO). ^{1}H NMR and FT-IR measurements were employed to characterize its chemical structure. The PES at various ratios was used to modify a bisphenol A epoxy resin (Ep828) by pre-reaction with curing agent 4,4′-diaminodiphenylmethane (DDM). The cured samples were investigated using differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA) and limited oxygen index (*LOI*). The results showed that the epoxy resins modified with PES exhibited higher glass transition temperatures (T_g), higher initial degradation temperatures (T_d 5 %) and better flame retardancy than the unmodified.

Key words: phosphorus-containing epoxide siloxane, epoxy resin, modification, thermal properties, limited oxygen index.

SYNTEZA NOWEGO ZAWIERAJĄCEGO FOSFOR POLISILOKSANU I ZASTOSOWANIE GO JAKO MODYFIKATORA WŁAŚCIWOŚCI TERMICZNYCH ŻYWICY EPOKSYDOWEJ

Streszczenie — W wyniku reakcji polimetylohydrosiloksanu (PMHS) z eterem glicydowym allilu (AGE) otrzymano epoksydowany siloksan, który następnie poddano reakcji, przebiegającej z otwarciem pierścienia, z 10-tlenkiem 9,10-dihydro-9-oksa-10-fosfafenantrenu (DOPO) uzyskując epoksydowany polisiloksan zawierający atomy fosforu (PES). Strukturę produktu potwierdzono metodami FT-IR i ^{1}H NMR (rys. 1 i 2). Za pomocą PES dodawanego w różnych ilościach modyfikowano żywicę epoksydową (Ep828) wstępnie poddawaną działaniu 4,4′-diaminodifenylometanu (DDM) (tabela 1). Właściwości termiczne otrzymanych próbek wyznaczano za pomocą różnicowej kalorymetrii skaningowej (DSC), dynamicznej analizy termomechanicznej (DMA) oraz analizy termograwimetrycznej (TGA) (tabela 2, rys. 4—7). W celu oceny palności próbek wyznaczono ich graniczne indeksy tlenowe (*LOI*, tabela 2). Stwierdzono, że próbki modyfikowane za pomocą PES charakteryzują się wyższą temperaturą zeszklenia (T_g), wyższą początkową temperaturą degradacji (T_d 5 %), a także obniżoną palnością w porównaniu z próbką niemodyfikowaną.

Słowa kluczowe: epoksydowany siloksan zawierający atomy fosforu, żywica epoksydowa, modyfikacja, właściwości termiczne, graniczny indeks tlenowy.

As an important industrial material, epoxy resin presents attractive characteristics, including low shrinkage on cure, good adhesion to substrates, and superior electrical and mechanical resistance [1]. Epoxy resins are widely used in many fields, especially in electronic industry. With the development of electronic technology, however, lack of heat resistance and flame retardancy of epoxy resin limits its usage in the field [2].

Considerable attention has been paid to increase flame retardancy of the epoxy resins [3—7]. Usually, halogen has been introduced to increase flame retardancy, but the method generates harmful halogenated gases. At present, introducing organophosphorous into the epoxy resin is the trend to avoid above disadvantages [3—5]. However, the organophosphorous flame retardant is always accompanied by a decrease in the initial decomposition temperature, which makes the epoxy resin unfit for the products requiring critical thermal stability. Moreover, due to the limit from chemical structures in molecular design during the introduction of organophosphorus, the low crosslinking density of the cured epoxy resins often cause poor heat resistance [7]. According to the previous report [8], the flame retardancy of phosphorus could be increased if providing an environment to reduce the thermal oxidation of phos-

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phorus char at the high temperature region. Organosiloxanes with many unique properties such as hydrophobic property, non-flammability, excellent thermal and thermo-oxidative stability, can meet the requirement of depressing thermal oxidation of phosphorus char [9]. Therefore, organosiloxane is considered to be an efficient modifier to increase the flame retardancy of epoxy resins. Besides, organosiloxane possessing numerous epoxide groups in the side chains of its backbone can improve heat resistance of epoxy resins by increasing the crosslinking density of the system. So phosphorus-containing epoxide siloxane (PES) could simultaneously enhance the heat resistance and flame retardancy of the epoxy resins.

In this paper, PES that contained phosphorus and epoxide moieties in the side chains of polysiloxane was synthesized. The PES at various ratios was used to modify the epoxy resin (Ep828) *via* a pre-reaction using 4,4′-diaminodiphenylmethane (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), dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA) and by determination of limited oxygen index (*LOI*).

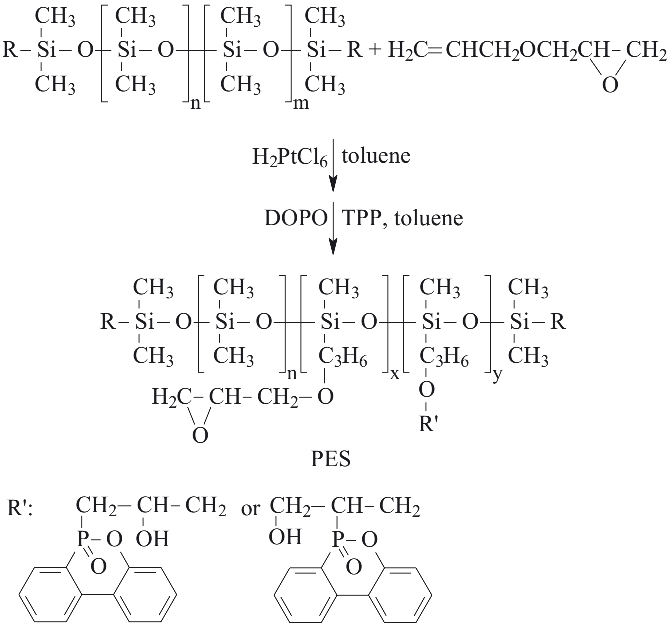
EXPERIMENTAL

Materials

9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) was available from TCI (Tokyo Chemical Industry, Japan). 4,4′-Diaminodiphenylmethane (DDM), triphenylphosphine (TPP) and hydrogen hexachloroplatinate hydrate (Pt-catalyst) were obtained from Aldrich Chemical Co. Allyl glycidyl ether (AGE) and polymethylhydrosiloxane (PMHS, characterized by molecular weight $\overline{M}_n$ = 6895 and 1.4 mol reactive proton per 100 g PMHS) were purchased from Xinghuo Chemical Co. of China. Diglycidyl ether of bisphenol A (trade name Ep828, characterized by epoxide equivalent weight *EEW* = 187 g/epoxide) was from Shell Chemical Co. All solvents were reagent grade or were purified by standard methods.

Synthesis of PES

21 g of PMHS, an excess of AGE (1.5 equivalents of Si-H) and 50 g of toluene were charged, under nitrogen atmosphere, into a 250 ml flask equipped with a stirrer and condenser. When the solution was heated to temp. 75 °C, Pt-catalyst in amount 0.01 wt. % per all reaction mixture was added to the flask and stirred until the reaction was completed [the disappearance of absorption peak of the Si-H (2156 cm^{-1}) in the infrared spectrum marked the completion of the reaction]. Epoxy siloxane (ES) was obtained by removing the excess of AGE and the solvent using a rotary evaporator. Subsequently, ES, DOPO (0.5 equivalents of epoxide group), triphenylphosphine as a reaction promoter in a concentration 0.2 wt. % per all reaction mixture and 60 g of toluene were orderly charged into another 250 ml flask. The mixture was allowed to reflux for 6 h and PES with *EEW* = 625 g/epoxide could be obtained by the solvent removing. The reaction mechanism is shown in Scheme A.



Scheme A. The synthesis of PES

Curing procedure of epoxy resins

100 ml of xylene, designated in Table 1 amounts of PES and DDM were introduced into a round-bottom flask. The mixture was allowed to react at temp. 150 °C for 5 h. After that, the solution was concentrated using a rotary evaporator and the prepolymer was obtained. Ep828 and prepolymer were stirred and melt blended at temp. 90 °C, and a vacuum oven was applied to remove air bubbles. Finally, the mixture was poured into a mold to produce the samples. The curing conditions were: 90 °C for 3 h, 150 °C for 2 h, and 180 °C for 1 h. After curing process was over, the cured products were demolded.

Table 1. Curing components of PES/DDM/Ep828 samples

Symbol of samples	Ep828, g	PES, g	DDM, g
Ep100/PES0	100	0	25.28
Ep95/PES5	95	5	24.39
Ep90/PES10	90	10	23.51
Ep85/PES15	85	15	22.63

Methods of testing

The chemical structure of PES was characterized by FT-IR and ^{1}H NMR methods. The FT-IR spectrum was recorded with RFX-65A FT-IR (Analect Co.). ^{1}H NMR was performed using a 400 MHz Brüker NMR spectrometer and $CDCl_3$ as a solvent.

Thermal properties of PES were determined by DSC, TGA and DMA methods.

The DSC measurements were performed using a Perkin-Elmer Pyris-1 thermal analysis apparatus under a dry nitrogen atmosphere with a heating rate of 10 deg/min. The TGA was performed by a Pyris-1 series thermal analyzer with a heating rate of 20 deg/min under both air and nitrogen atmosphere. DMA measurements were carried out using a dynamic mechanical analysis apparatus (TA DMA 2980), specimens (2 × 8 × 30 mm) were tested in a three-point bend mold, the thermal transitions were studied in the range from 50 to 220 °C with a heating rate of 5 deg/min and fixed frequency of 10 Hz.

The *LOI* values were measured using a ZRY-type instrument (China) with a test specimen bar of 120 × 6 × 3 mm according to the standard "oxygen index" test ASTM D-2863-77.

RESULTS AND DISCUSSION

Synthesis of PES and determination of its structure

ES was obtained *via* the hydrosilylation reaction [10]. Owing to the -P-H group of DOPO showing high reactivity toward oxirane group, the reaction has been widely applied to the preparation of DOPO derivatives [4]. Through the reaction between the -P-H group and the oxirane group, a kind of DOPO-containing siloxane was synthesized (Scheme A). FT-IR spectrum of PES obtained is shown in the Fig. 1. The disappearance of the peak at 2384 cm^{-1} (-P-H) and the appearance of the peak at 3430 cm^{-1} (-OH) indicate that the DOPO completely reacts with the ES. The appearances of the peaks at 1587 cm^{-1} (Ph), 1466 cm^{-1} (P-Ph) and 1203 cm^{-1} (P=O) imply that the PES contains cyclic DOPO structure.

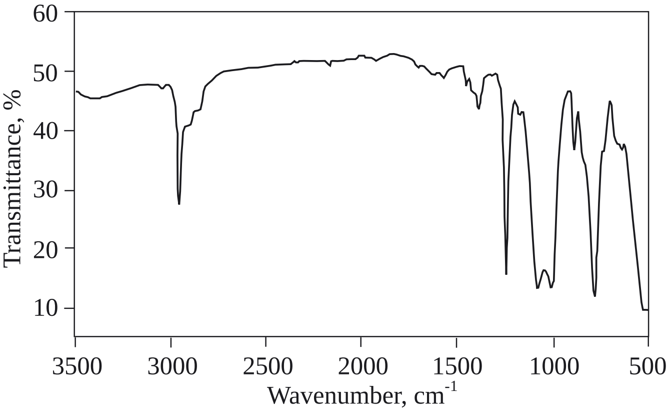


Fig. 1. FT-IR spectrum of PES

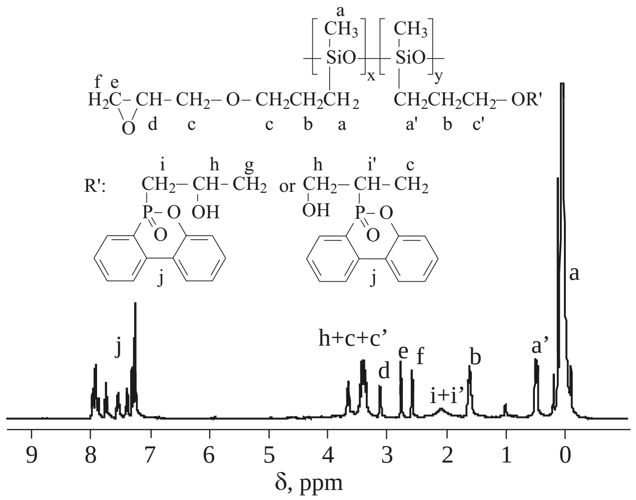


Fig. 2. ^{1}H NMR spectrum of PES

The structure of PES was further confirmed with ^{1}H NMR (Fig. 2). The reaction between P-H and oxirane group might lead to the formation of two kinds of groups [-P-CH_2-CH (OH)- and $HOCH_2CH$ (P)-] by means of α and β addition. Both groups are observed in the ^{1}H NMR spectrum of PES, the peak at δ = 1.98—2.21 ppm is attributed to the mentioned two groups, which demonstrates the occurrence of the addition reaction between the P-H and oxirane ring. Chemical shift δ = 7.24—7.99 ppm belongs to the eight aromatic protons of the biphenyl section and the resonance peak at δ = 8.79 ppm attributes to the disappearance of P-H. The results are in good agreement with those of the FT-IR.

DSC and DMA analyses of the cured epoxy resins

Glass transition temperatures (T_g) of the epoxy resins cured with DDM were measured using DSC and DMA. The results are listed in Table 2 and are presented in Figs. 3 and 4, respectively. It could be easily observed that T_g

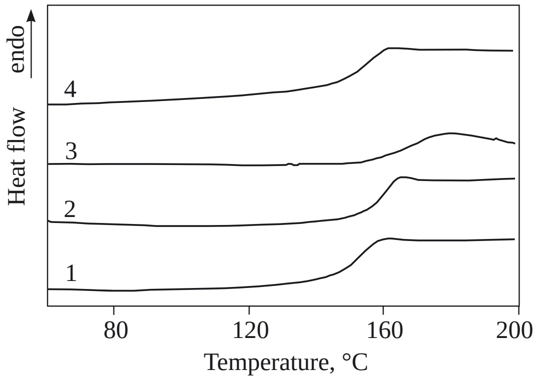


Fig. 3. DSC curves of the samples: 1 — Ep100/PES0, 2 — Ep95/PES5, 3 — Ep90/PES10, 4 — Ep85/PES15; designations of samples — see Table 1

T a b l e 2. Thermal behavior data of the cured epoxy resins containing PES at various ratios; description of the symbols in the text

Symbol of samples	PES content, wt. %	T_g, °C		T_d 5 %, °C		Char yield at 720 °C		*LOI*
		by DSC	by DMA	under N_2	under an air	under N_2	under an air	
EP100/PES0	0	152.5	160.2	342.9	336.8	18.4	6.0	22
EP95/PES5	5	159.2	167.4	345.7	342.2	21.7	19.4	23
EP90/PES10	10	166.4	177.7	354.0	353.1	23.9	22.3	25
EP85/PES15	15	153.6	161.6	362.5	363.8	24.8	25.1	27

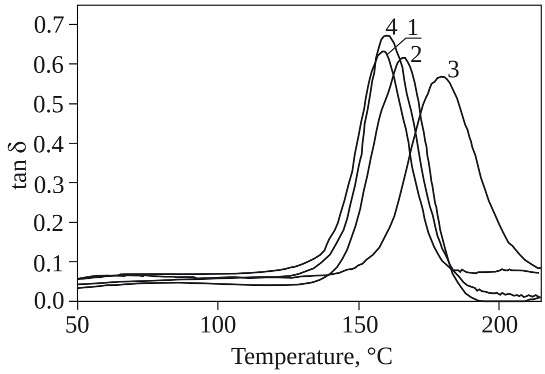


Fig. 4. DMA results as damping coefficient (tan δ) relaxations of the cured epoxy polymers; description of curves as in Fig. 3

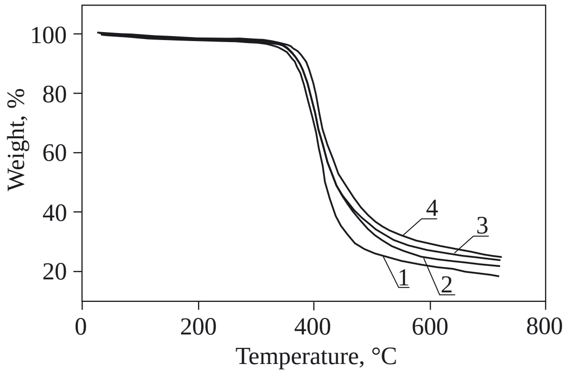


Fig. 5. TGA curves of the cured epoxy samples determined under N_2 atmosphere; description of curves as in Fig. 3

initially increased with increasing in PES content, then decreased when the content of PES reached 15 wt. % (Figs. 3 and 4). The modified epoxy resin containing 10 wt. % of PES had a maximal T_g of 166.4 °C (by DSC), which was about 14 deg higher than that of the neat cured epoxy resin. When the content of PES reached 15 wt. %, T_g of modified epoxy resin decreased to 153.6 °C (by DSC). This phenomenon could be explained by the fact that PES with many epoxide groups in its side chains in low content range could react with DDM and enter into the crosslinking network of the cured epoxy resin, which could function as the crosslinking sites to some extent and led to a higher crosslinking density and consequently higher T_g. In addition, the bulky rigid DOPO groups hindered the free movement of polymeric chains, which also resulted in the increase in T_g [4, 5]. When the content of PES exceeded a certain value, the siloxane chains would not be well dispersed in the continuous epoxy resin matrix due to the difference of their polarities. The increase in crosslinking density could not compensate for the plasticization of PES and consequently led to the depression of T_g.

TGA of the cured epoxy resins

The TGA curves of the cured polymers under air or nitrogen atmosphere are shown in Figs. 5 and 6, respectively, and the details of the results are presented in Table 2. The initial degradation temperature of the cured samples, taken at 5 wt. % weight loss temperature (T_d 5 %), rised up after PES was incorporated, which indicated that introducing the DOPO-containing multi-epoxy siloxane could improve the thermal stability of epoxy resins. Meanwhile, the residual weight increased with the increase in PES content. The thermal degradation rate in high temperature region decreased because of the formation of phosphorus-char and silicon-rich residue on the matrix surface [11].

It has been reported that high char yields was connected with high flame retardancy [12]. As to the modified epoxy resins, the char formation rate of the epoxy resins at 720 °C was increased when PES was incorporated into the epoxy resin systems, as shown in Table 2. TGA of the resins performed under air or N_2 atmosphere showed that, char-formation rates were obviously higher than that of the neat epoxy resin. The char-formation rate under air atmosphere of modified epoxy resin containing 15 wt. % of PES was about 4 times higher

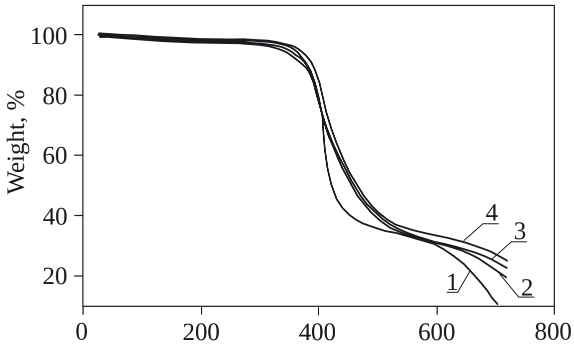


Fig. 6. TGA curves of the cured epoxy samples determined under air atmosphere; description of curves as in Fig. 3

than that of the neat epoxy resin, which indicated that PES improved the flame retardancy of the epoxy resins. It was interesting to note that the char-formation rate under air was different and slightly higher than that under N_2 atmosphere when the content of PES was 15 wt. %. One possible reason was that too many DOPO-containing multi-epoxy silicones would form more silicon oxides in an air [11, 13].

In order to further testing of the flame-retardant properties of these cured epoxy resins, the *LOI* values were measured and the results were shown in Table 2. With the incorporation of PES into the epoxy compositions, the *LOI* of the epoxy resin rised from 22 for the unmodified epoxy resin to 27 for the sample Ep85/ PES15, which also demonstrated an improvement in the flame retardancy of the modified epoxy resins. From the discussions above, we could safely draw a conclusion that the epoxy resins modified with PES exhibited higher thermal stability and better flame retardancy and were superior in comparison to those phosphorus-containing epoxy resins reported [14].

CONCLUSION

PES containing DOPO and epoxide groups was introduced into EP828 to prepare a novel cured epoxy system *via* the pre-reaction of PES and DDM. The chemical structure of PES was confirmed by FT-IR and ^{1}H NMR. DSC and DMA studies showed that T_g of the modified epoxy resins first increased with increasing PES content, then decreased when the content of PES reached 15 wt. %. The modified epoxy resin containing 10 wt. % of PES had a maximal T_g of temp. 166.4 °C determined by DSC, which was about 14 deg higher than that of the neat cured epoxy resin. The results of TGA measurements and *LOI* values indicated that T_d 5 % and flame retardancy of the epoxy resins increased with the increase in PES content.

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