Silylation of epoxidized soybean oil with triethoxysilanes, synthesis and characterization of their polyurethanes

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Abstract: Silylation of epoxidized soybean oil (ESBO) was carried out by epoxy ring opening reaction of methoxy and ethoxy silane compounds. ^{1}H NMR and FTIR spectra confirmed that two novel bio-based polyols, PSiTh and PSiAm, were obtained through the ring opening of epoxy by the mercapto and amino moieties of MPTMS and APTES, respectively. Polyurethanes of these polyols were prepared using $4,4^{'}$ - methylene-bis(phenyl isocyanate) (MDI) to incorporate silanol groups into polymer network and were labeled as PUSiTh and PUSiAm, respectively. To see the impact of silanol and phosphorous groups on flame retardant properties, the chain extended polyurethanes, PUSiThCE and PUSiAmCE were also prepared with bisphenol-A bis (hydroxy phenyl phosphonate) (BABHPP). Polyurethanes bearing thio-ether bonds besides alkoxy silane groups were characterized using FTIR spectroscopy. Prepared foams exhibited significant thermal stability and flame retardant properties with a limiting oxygen index (LOI) of 22-24%. Chain extended polyurethanes had 11-13 % higher LOI value than the corresponding non-chain extended polyurethanes.

Key words: silylation, biobased, polyurethane, foam, flame retardant

1. Introduction

Functional trialkoxysilanes $(RSi(OR)_3)$ are used as coupling agents in some applications to improve adhesion between polymeric matrices and inorganic substrates [1,4]. $RSi(OR)_3$ s have two types of reactive functionality, on one side alkoxy groups (OR) can hydrolyse to silanol containing species and then form hydrogen bonds/covalent bonds with substrates bearing OH groups, on the other side organic functional groups (R') such as amine, thiol, vinyl or phenyl react with other organic matrices or inorganic substrates [5,7].

Silicon is introduced into polymer networks such as epoxy resins or polyurethanes through several polymerization methods including living anionic polymerization, ring opening polymerization, atom transfer radical polymerization and step-growth polymerization [8-14] to enhance properties such as flame retardance, elasticity, biocompatibility and thermal and oxidative stability. Polyurethanes made up of hard and soft segments, find a variety of applications such as surface coatings, biomedical devices, foams, elastomers, composites and adhesives, due to the presence of hard and soft segments that give good elastic and reasonable mechanical strength [15-20]. In recent years there is an increased focus on converting renewable resources into polymers, plasticizers and chemicals for industry to answer ecological concerns, reduce the consumption of fossil resources and design new chemical patterns in line with green chemistry practices [21-23]. One of the most versatile and

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consumed biopolymer is polyurethane [24-27]. Vegetable oil based polyols are the major components of biobased polyurethanes as renewable resources that can compete in many ways with polyols derived from petrochemical sources due to their sustainability, availability and value addition to agricultural products [28-32]. Many routes to prepare vegetable based polyols have been reported in the literature such as transesterification, ozonolysis followed by hydrogenation, epoxidation followed by hydroxylation and thiolene coupling [33-35]. One of the routes for hydroxylation of epoxidized vegetable oils, that is, polyol formation, is epoxy ring opening reaction with several reagents bearing functional groups such as alcohols, thioalcohols, carboxylic acids, amines and halogenated acids [36-40]. Silylation of unsaturated vegetable oils using trimethoxysilane and then the synthesis of its polymer with polydimethoxysilane was reported in literature [41]. The synthesis of silicon based polyurethanes with good mechanical properties, improved biocompatibility, bio and thermal stability were achived by incorporation of linear polyhedral oligomeric silsesquioxane (POSS) into the polymer or chain extension with silicon containing chain extenders. Silylation of soybean oil (SBO) was reported previously by Narayan and coworkers with "ene reaction" by grafting vinyl trimethoxysilane (VTMS) onto double bounds of triglyceride chain [42-43].

The aim of this work was to prepare silicone containing biobased polyurethane. The strategy involved first the introduction of silicone atom into epoxidized soybean oil by silylation of epoxidized soybean oil (ESBO) and then copolymerization of the resulting triglyceride with 4,4´ - methylene-bis(phenyl isocyanate) (MDI).

In this study, the silylation of ESBO was carried out for the first time by ring opening of epoxy with silanol coupling agents. 3-mercaptopropyltrimethoxysilane (MPTMS) and aminopropyltriethoxysilane (APTES) were used for the epoxy ring opening reaction. At the end of this reaction, two novel silicon containing soybean oil based polyols, 3-mercaptopropyltrimethoxysilane (MPTMS)-based polyol (PSiTh) and 3-aminopropyltriethoxysilane (APTES)-based polyol (PSiAm) were synthesized. Polyurethanes of these polyols were also prepared. Characterization of polyols were performed using proton and carbon nuclear magnetic resonance (^{1}HNMR and ^{13}CNMR) spectroscopy, fourier transform infrared spectroscopy (FTIR) and gel permeation chromatography (GPC). Thermal characteristics and flame retardant properties of the polyurethane foams were studied using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and limiting oxygen index (LOI) measurement.

2. Results and discussion

The proposed reaction route for silylation of ESBO with 3-mercaptopropyltrimethoxysilane (MPTMS), 3-Aminopropyltriethoxysilane (APTES), prepolymers of PUSiTh, PUSiAm and the structures of chain extended polyurethanes were presented in Figure 1, Figure 2, Figure 3 and Figure 4.

2.1. FTIR spectra of polyols (PSiTh, PSiAm) and polyurethanes (PUSiTh and PUSiAm)

FTIR spectra of ESBO and polyols (PSiTh and PSiAm) can be seen in Figure 5. Disappearance of epoxy peak at 830 cm^{-1} and appearance of new hydroxyl peaks at 3450cm^{-1} suggest that silylation of ESBO took place over the ring opening reaction. The disappearance of thiol (SH) peak at 2545 cm^{-1} belonging to MPTMS confirms the ring opening reaction. The overlapping of methylene asymmetric stretching of triglyceride and asymmetrical streching of Si-OCH$_3$ is observed at 2925-2854 cm^{-1} [44]. The other peak of Si-OCH$_3$ appears at 811cm^{-1}. The absence of of NH$_2$ peak at 1570 cm^{-1} and the appearance of N-H scissoring and symmetric peaks at 1650 and 1543 cm^{-1} and C-N peak at 1239 cm^{-1} suggest that silylation occured through the ring opening of
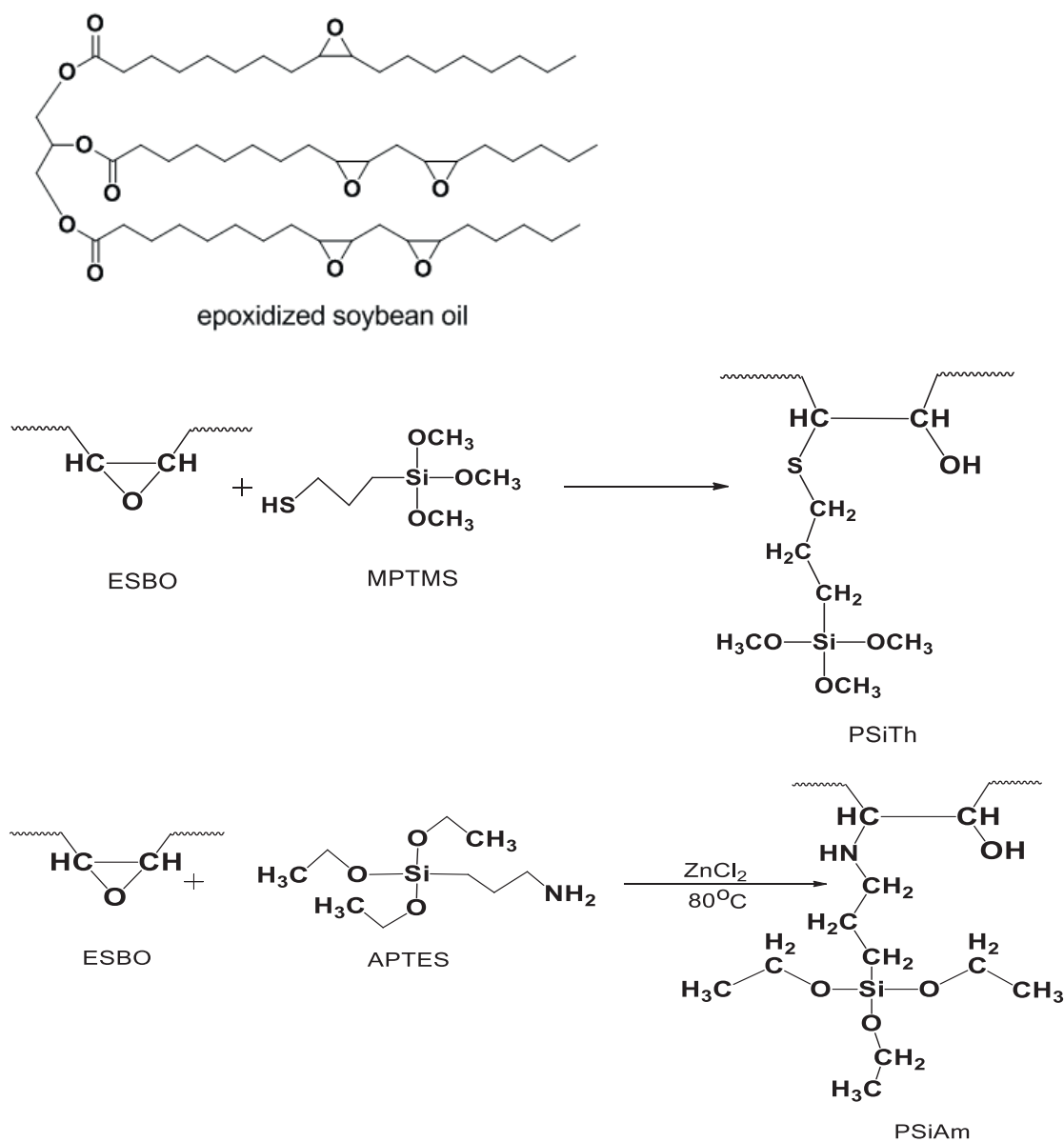
Figure 1. Ring opening reaction of ESBO with (3-Mercaptopropyl)trimethoxysilane and (3-Aminopropyl)triethoxysilane

epoxy by amine group of APTES. SiO-CH_2 and Si-O-C_2H_5 stretching vibration peaks appeared at 1239 and 956 cm^{-1}, respectively. The other important peaks are:1741 cm^{-1} (triglycerides carbonyl stretching), 1459 cm^{-1} (CH_2 bending vibration), 1379 cm^{-1} (CH_3 bending vibration), 1161 cm^{-1} (stretching vibrations of C-O group in esters), 734 cm^{-1} (CH_2 rocking vibration) [45-48]. The peaks of polyurethanes were observed at 3299-3327 cm^{-1}, 1501-1511cm^{-1}, 1210-1240 cm^{-1} (N-H stretching), 1595-1598 cm^{-1}(-C=O stretching vibrations). The occurence of peak at 1438-1439 cm^{-1} due to aromatic C=C stretching vibrations of BABHPP, indicates that chain extension took place.
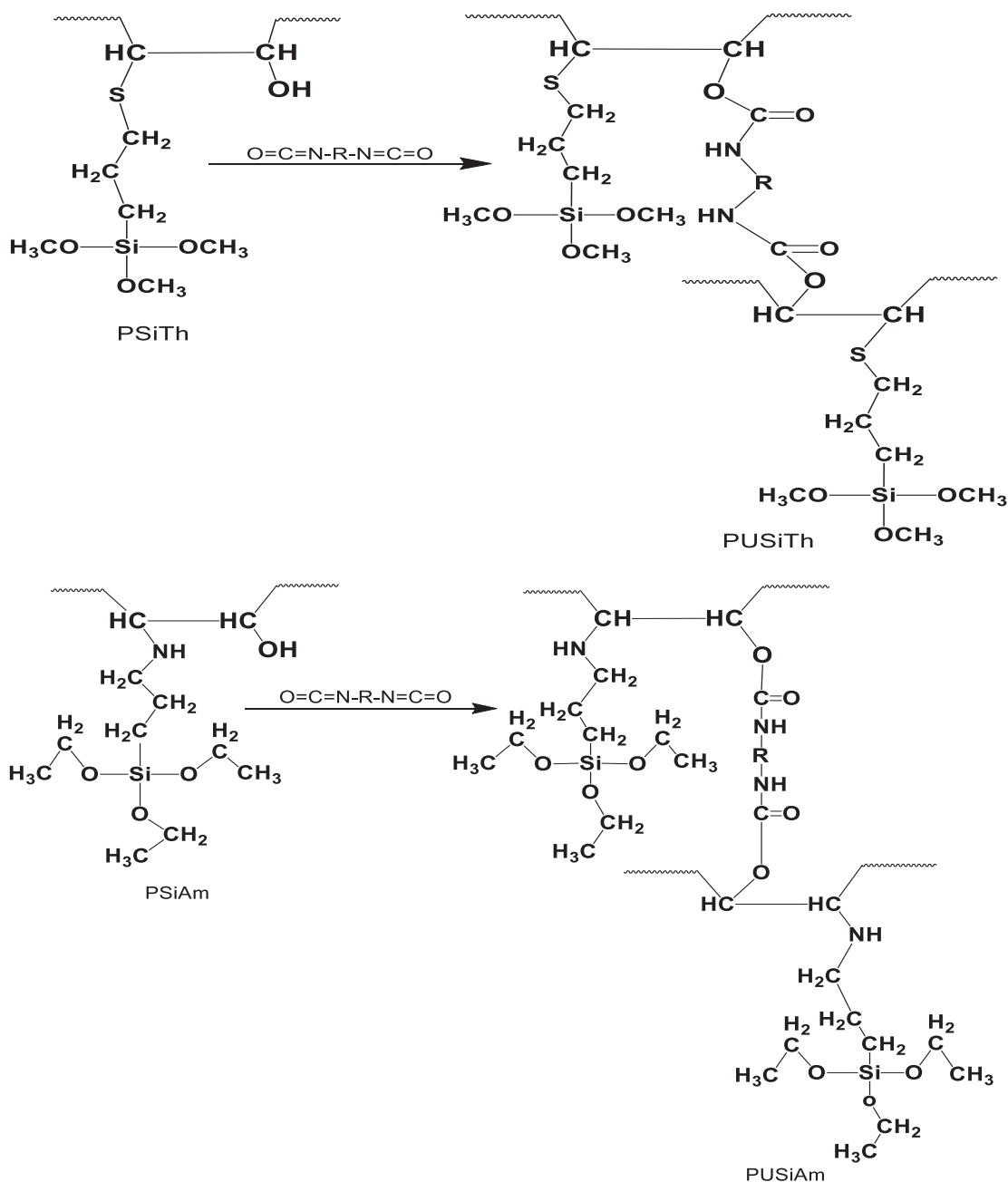
Figure 2. Proposed route for polyurethane reactions

2.2. NMR spectra of silylated polyols (PSiTh, PSiAm)

^{1}H NMR spectrum of synthesized PSiTh and PSiAm are illustrated in Figure 6. The spectrum of ESBO was included for comparison. The signals at 5.2-5.4 ppm and 3.4 ppm attributed to O**H** and –C**H**-OH protons, respectively, reveals that the ring opening of epoxy occured and that O**H** group was formed. The presence of C**H₃** protons of Si-O-C**H₃** at 3.5 ppm and C**H₂** protons of **-**S-CH$_2$-CH$_2$-CH$_2$-Si- at 0.80 ppm is the evidence of silylation by MPTMS. The peaks at 2.49 ppm and 2.99 ppm attributed to -NH-C**H₂** and N**H-**CH**₂**, respectively, indicate that silylation took place through amine function of APTES. In the ^{13}C NMR, the presence of peaks
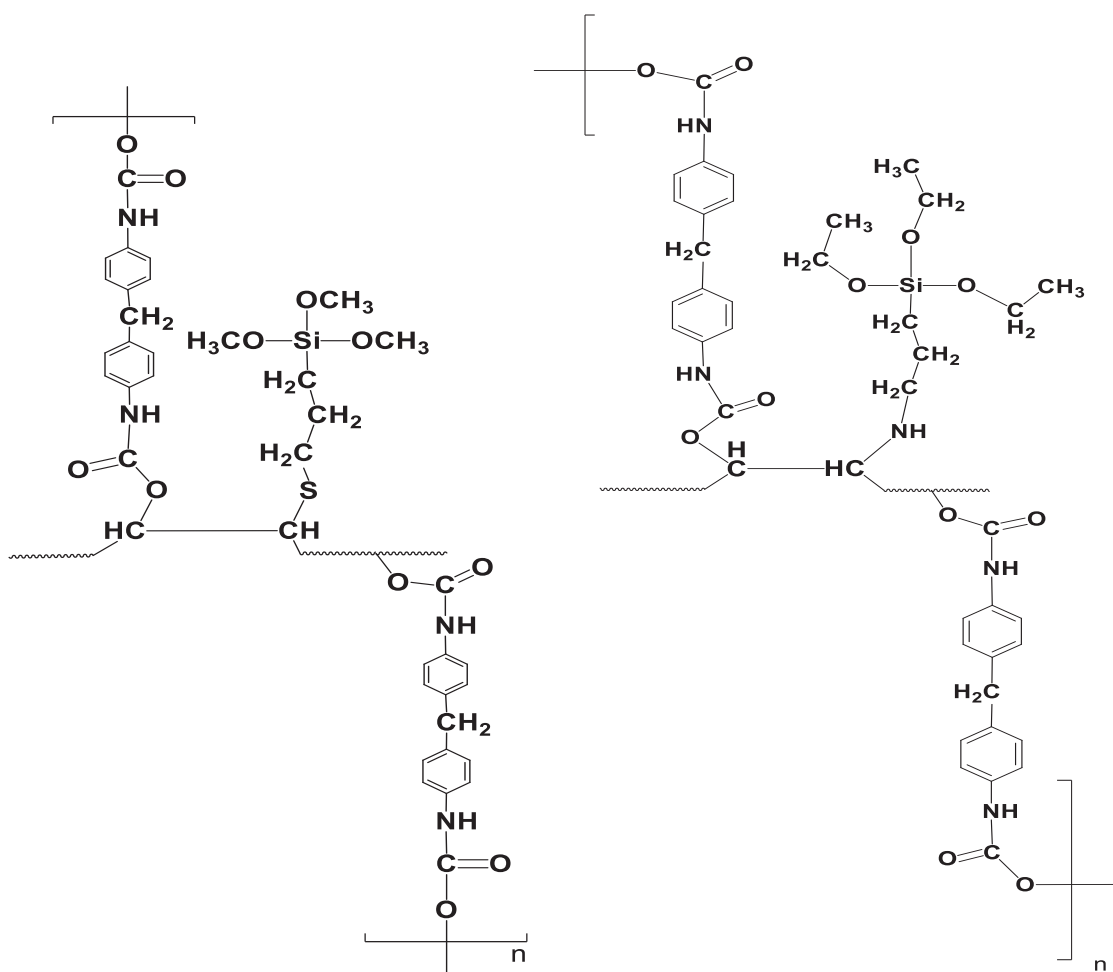
Figure 3. Prepolymer structure for PUSiTh (left), PUSiAm (right)

at 56 ppm (carbons adjacent to OH), 13 ppm (carbons of Si-**CH**$_2$) for both polyols, 50 ppm (carbons of -Si-O-**CH**$_3$ – of PSiTh) **,** 58 ppm (carbons of –O-**CH**$_2$), 27.1 ppm (carbons of glycerine backbone of -CH$_2$-**CH**$_2$-CH$_2$), 14.42 ppm (carbons of CH$_2$-**CH**$_3$), 13 ppm (carbons of Si-**CH**$_2$), confirmed successful silylation (Figure 7).

2.3. Differential scanning calorimetry analysis.

Thermal transition temperatures of silylated polyols and polyurethanes were measured by differential scanning calorimetry (DSC). As seen in Figure 8, glass transition and crystallization were observed for both polyols. The presence of different crystalization temperatures can be attributed to the formation of different crystalline structures resulting from hydrogen bonding of OH groups. Polyurethanes exhibited glass transition only and the absence of melting points indicates that PU reaction ook place. Chain extended polyurethanes showed slightly higher glass tansition temperatures due to the rigidity of phenyl phosphonic group of BABHPP used as chain extender (Table 1).

2.4. Thermogravimetric analysis

It can be seen in Figure 9 that the thermal stability of PSiTh and PSiAm increases as their OH numbers increase. The first decomposition starting at 140 and 193 ^{o}C, respectively, may be due to the cleavage of
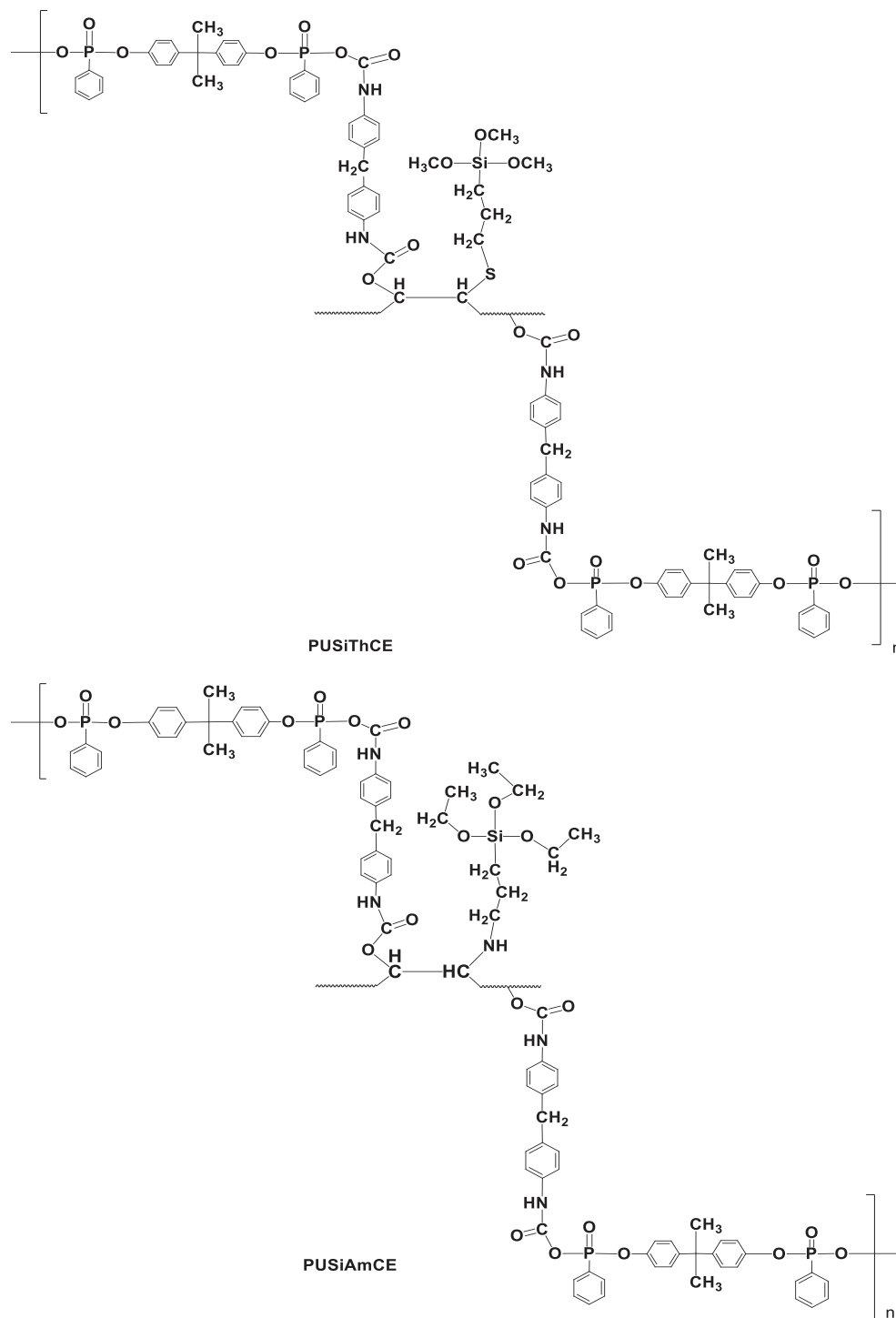
Figure 4. Structures of chain extended polyurethanes, PUSiThCE (top) and PUSiAmCE (bottom)

recinoleic moiety (C=C) present in polyols which comes from the non-epoxidized double bonds of ESBO. The second decomposition of both polyols was started at 345-407 ^{o}C corresponding to full decomposition. This is due to intramolecular attractions between epoxy and carbonyl group through hydrogen bonding, polar-polar
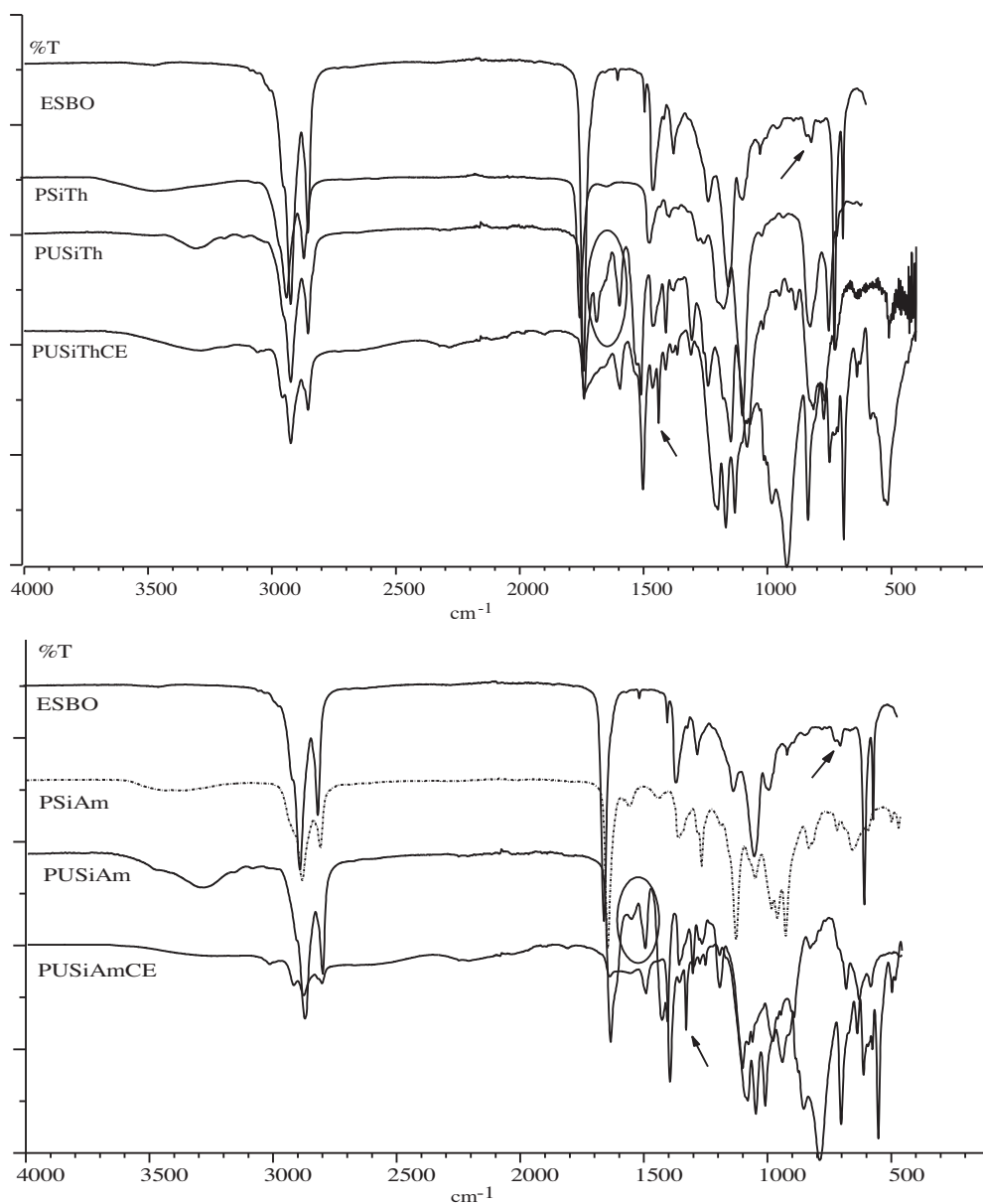
Figure 5. FTIR spectra of PSiTh, PUSiTh, PUSiThCE (top) and PSiAm, PUSiAm, PUSiAmCE (bottom)

interactions which makes the structure more rigid [49]. Thermal degradation of PUSiTh and PUSiAm occured at 2 or 3 stages. First step is the onset temperature where the decomposition of weak urethane bonds takes place at 221 and 246 ^{o}C for PUSiTh and PUSiAm, respectively. This decomposition stems from the dissociation to isocyanates and alcohols, the formation of primary amines and olefins, or the formation of secondary amines. The second decomposition temperature observed at 320 - 398 ^{o}C for PUSiTh and 317 ^{o}C for PUSiAm can be attributed to dehydrogenation of alkyl groups present in polyol. The third step of degradation observed at 462 and 455 ^{o}C in the thermograms of PUSiTh and PUSiAm, respectively was due to the degradation of remaining components of polyurethane [50].
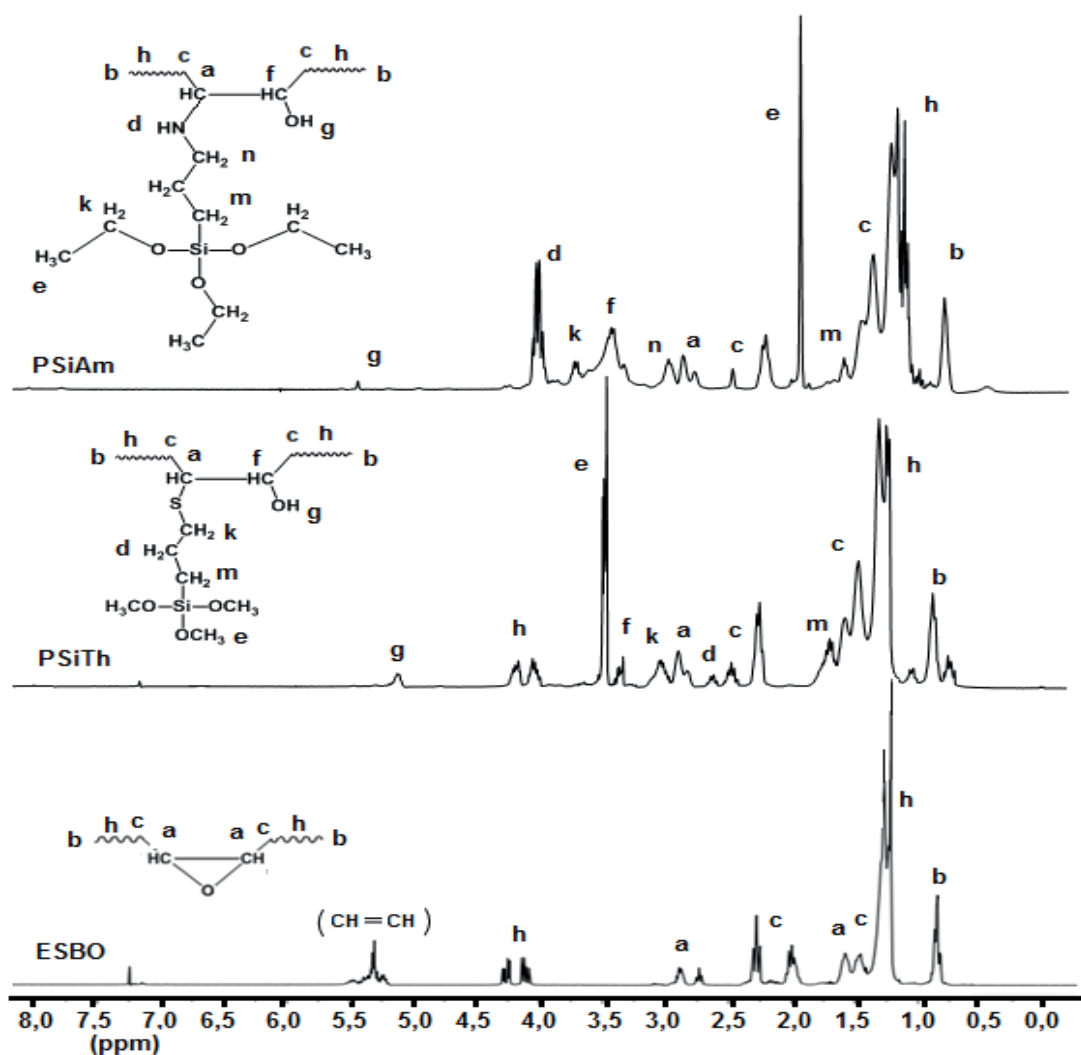
Figure 6. ^{1}H NMR spectra of ESBO, PSiTh and PSiAm

Table 1. DSC results of polyols and polyurethanes

Table 1. DSC results of polyols and polyurethanes		
Sample	T_g (^oC)	T_c(^oC)
PSiTh	-42, -12, 18	2
PSiAm	-72, -24	-38, -28
PUSiTh	-32,-10, 60	
PUSiAm	-22, 38	
PUSiThCE	40	
PUSiAmCE	12	

2.5. Morphological study of polyurethanes

The crystallinity of polyurethanes was investigated using X-Ray diffraction analysis. As can be seen in Figure 10, a broad peak centered at $2\Theta=20^o$ and the absence of sharp peak reveals that both polyurethanes have
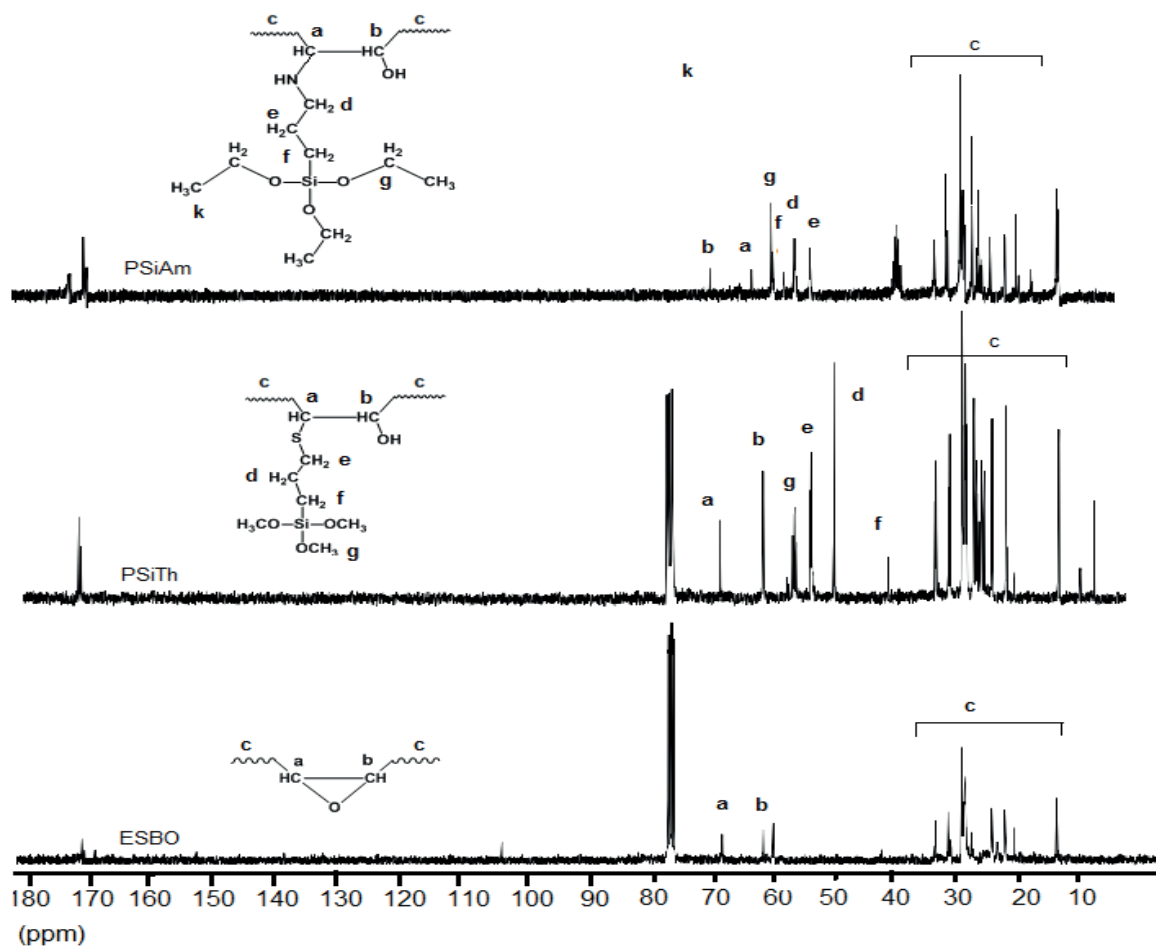
Figure 7. ^{13}C NMR spectra of ESBO, PSiTh and PSiAm

amorphous structure. In addition to this, the peak of PUSiTh is broader than that of PUSiAm in line with DSC thermogram, which indicated lower Tg.

Cell structure of silylated rigid polyurethane foams was studied under scanning electron microscopy. The SEM analysis exhibited that both polyurethane foams had honeycomb cell structure with closed cells. As seen in Figure 11, there was some degree of inhomogeneity in between cells which may be due to the presence of phase separation originated from soft and hard segments.

Energy Dispersive X-ray Spectroscopy (EDS) analysis was conducted to investigate the presence of sulfur, silicone and phosphorous elements in silylated polyols and P-chain extended polyurethanes. Single measurement was taken in 1 mm^2 of area at a depth of 10-15 μ. The analysis indicated that MPTMS and APTES were bonded to ESBO by epoxy ring opening and that silylation was successful. The chain extension of PUSiTh and PUSiAm with BABHPP was confirmed by the presence of phosphorous. The weight percent of each expected element as measured by EDS were given in Table 2.

2.6. Flame retandancy of polyurethanes

Limiting oxygen index (LOI) test is performed to evaluate the burning characteristics of chain extended and non-chain extended silicon containing polyurethanes. LOI is defined as the minimum concentration of oxygen,
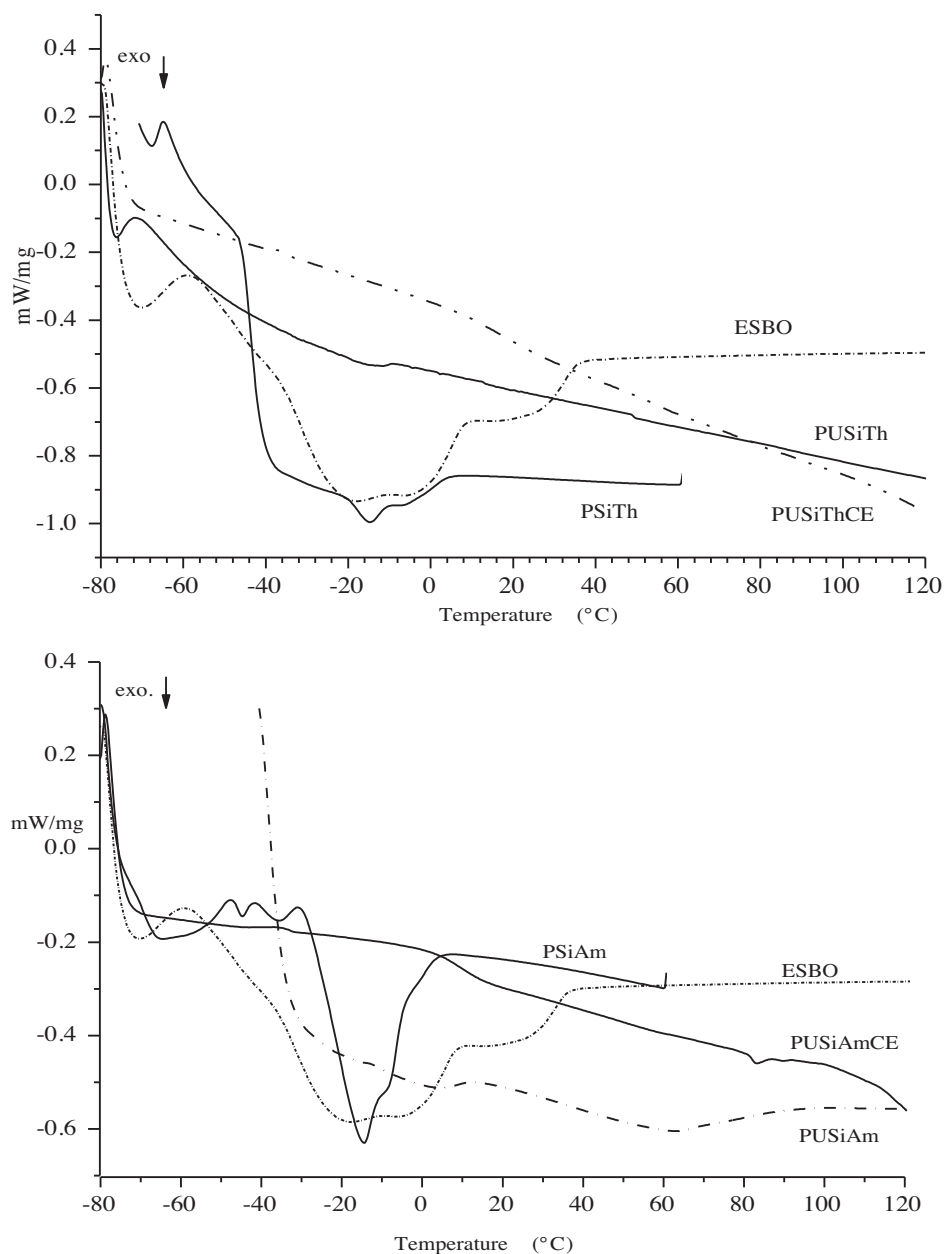
Figure 8. DSC thermograms of ESBO, PSiTh, PUSiTh and PUSiThCE (top), ESBO, PSiAm, PUSiAm and PUSiAmCE (bottom)

in a mixture of oxygen and nitrogen that will support combustion of a test specimen and is expressed as volume percentage. Burning times t_1 and t_2 which were the first and the second burning times, respectively, after the flame source was removed were indicated in Table 3 along with the LOI values and dripping behavior of each specimen. Photos of char residues of polyurethanes after the candle-like combustion test can be seen in Figure 12. PUSiTh and PUSiAm had LOI values of 23.6% and 22.8%, respectively. The existence of Si in polyurethanes by 5.3 wt% and 7.5 wt%, as measured by EDS, raised the LOI value by 14.6 % and 10.6% as compared to non-silicone containing bio-based polyurethanes which were reported to have LOI values of 18-20% [51]. By the introduction of phosphorous into the polymer structure by 18.4 wt% and 18.1 wt% via the chain
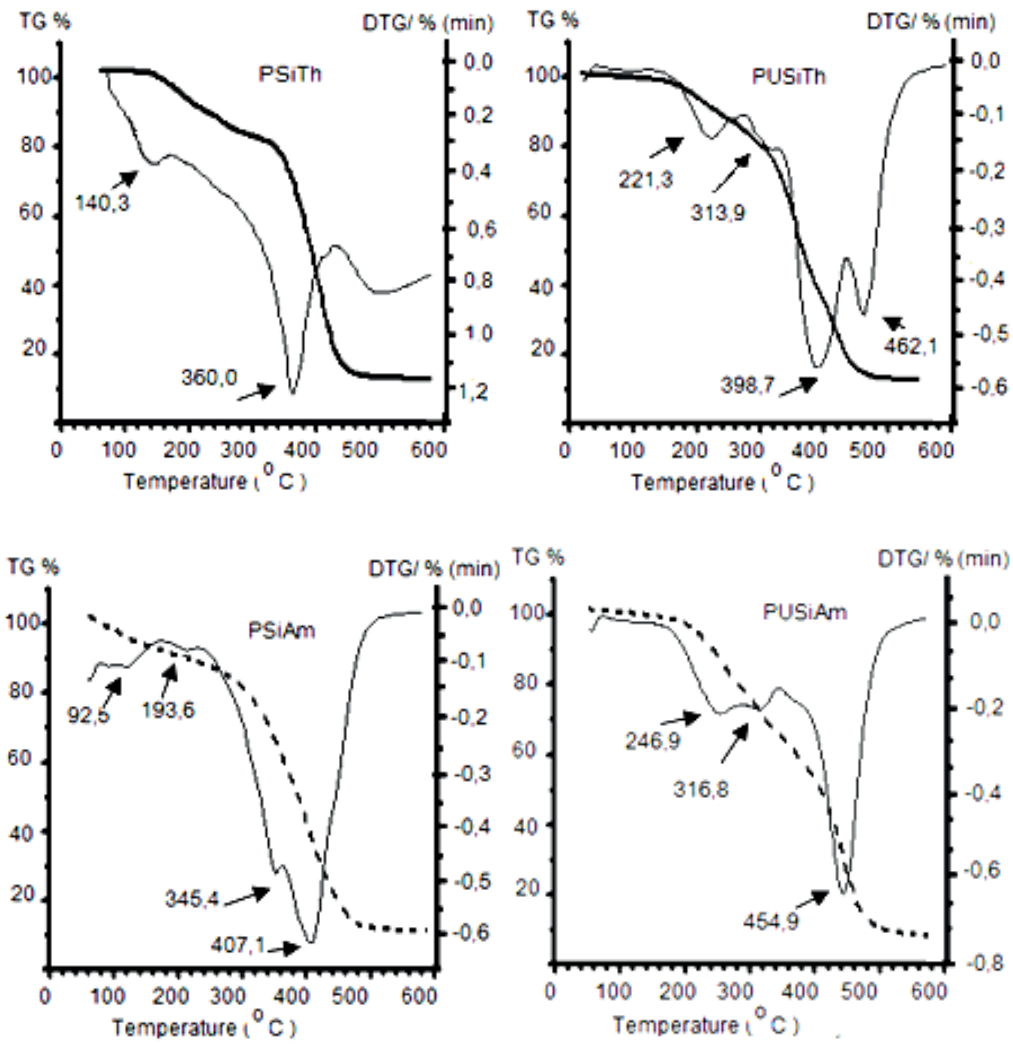
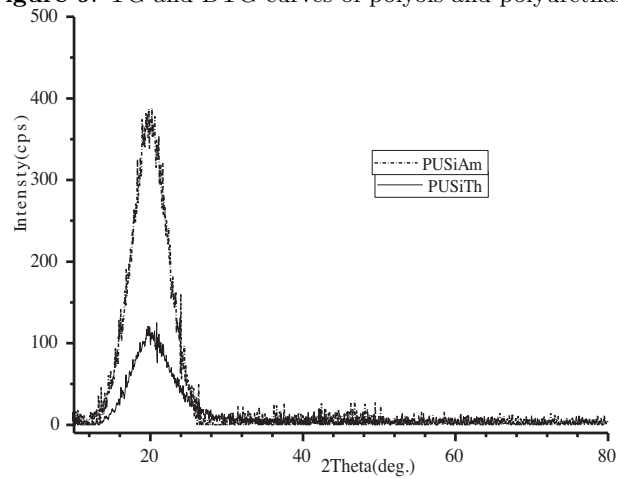**Figure 9**. TG and DTG curves of polyols and polyurethanes
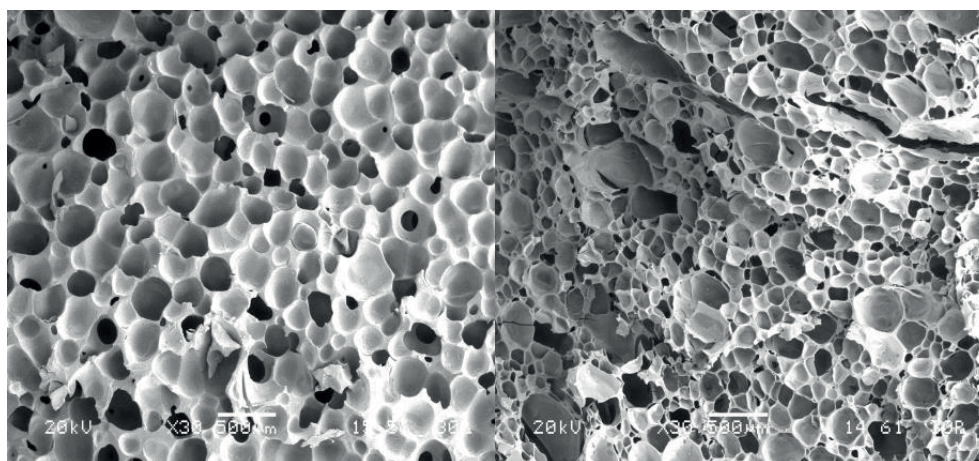

Figure 10. X-ray diffractograms of PUSiTh and PUSiAm

Figure 11. SEM micrograph of PUSiTh (left), and PUSiAm (right)

Table 2. EDS analysis of chain extended polyols

Element	Wt %	
	PUSiThCE	PUSiAmCE
C	51.63	54.20
O	20.75	19.72
Si	5.32	7.92
P	18.42	18.10
S	4.34	-

extender, LOI values increased from 23.6% to 26.3% and 22.8% to 25.6% for PUSiTh and PUSiAm, respectively. In addition to the increase of LOI, chain extension decreased the burning time of polyurethanes from 15 s to 9 s for PUSiTh and 30 s to 8 s for PUSiAm.

Table 3. LOI values and UL-94 classification of polyurethane foams

Sample codes	UL-94	Burning time(s)		Dripping	LOI(%)
		t_1	t_2		
PUSiTh	V-1	2	15	No	23.6
PUSiAm	V-1	-	30	No	22.8
PUSiThCE	V-0	2	9	Yes	26.3
PUSiAmCE	V-0	-	8	Yes	25.6

2.7. Foam properties

The compression strengths of the prepared foams which depend on cell size, foam density and polyol functionality were measured as 57.63 kPa and 157.34 kPa at 50% compression for PUSiTh and PUSiAm, respectively. The corresponding foam densities were found to be 268 kg/m^3 and 274 kg/m^3. The higher foam density of PUSiAm can be attributed to its higher OH functionality compared to PUSiTh.

Figure 12. Photographs of char residues from (a) PUSiTh, (b) PUSiAm after LOI test

3. Experimental

3.1. Materials

Aminopropyltriethoxysilane (APTES), 3-mercaptopropyltrimethoxysilane (MPTMS), epoxidized soybean oil and 4,4´-methylenebis(phenyl isocyanate) (MDI), bisphenol-A (BPA), phenyl phosphonic dichloride (PPDC) were purchased from Sigma-Aldrich, zinc chloride, methylene chloride, and sodium bicarbonate were purchased from Merck KGaA, Germany. All of these chemicals were used as received.

3.2. Silylation of epoxidized soybean oil with (3-mercaptopropyl)trimethoxysilane (MPTMS)

ESBO was silylated in a 250 ml, round-bottomed-flask equipped with a reflux condenser, a stirrer and a thermometer. MPTMS (4.23g, 0.021 mol) was added slowly under nitrogen atmosphere to the solution of ESBO (12.0 g, 0.013 mol) in 100 ml of ethyl acetate in two hours. The mixture was stirred for 24 hours at 45 ^{o}C, and then neutralized with sodium bicarbonate solution. The organic phase was dried with anhydrous magnesium sulfate and then the solvent was removed at a rotating vacuum evaporator. A viscous liquid was obtained with 78% yield. The hydroxyl value of the resulting polyol was 261.53 mg KOH/g.

3.3. Silylation of epoxidized soybean oil with (3-Aminopropyl)triethoxysilane (APTES)

Silylation reaction of (3-Aminopropyl)triethoxysilane was performed using a three necked, 250 ml, round-bottomed-flask equipped with a reflux condenser, a stirrer and a thermometer. ESBO (12.0 g, 0.013 mol) was dissolved in APTES (4.64 g, 0.021 mol) and then ZnCl$_2$ (0.30 g, 0.002 mol) was added to this mixture to initiate the reaction. The mixture was stirred under nitrogen atmosphere for 4 hours at 80 ^{o}C and then 300 ml of ethyl acetate was added to the mixture at room temperature. The solution was washed with sodium bicarbonate solution for neutralization. The organic phase was dried with anhydrous magnesium sulfate and

then solvent was removed at a rotating vacuum evaporator. A viscous liquid was obtained with 81% yield. The hydroxyl value for the resulting polyol was 280.29 mg KOH/g.

Hydroxyl number and viscosity of the synthesized polyols are listed in Table 4.

Table 4. OH number and dynamic viscosity of polyols and BABHPP

Table 4. OH number and dynamic viscosity of polyols		
Samples	OH Number (mg KOH/g)	Viscosity (mPa.s)
ESBO	-	38
PSiTh	261.53	243
PSiAm	280.29	151

3.4. Preparation of polyurethanes from MPTMS-based polyol (PSiTh) and APTES based polyol (PSiAm)

Polyurethanes of the synthesized polyols were prepared with one-pot, prepolymer hand mixing method without solvent and catalyst. In one-pot method, typically 0.3 g of MDI was melt at 50 ^{o}C and then 1.0 g of PSiAm and 20 mg of deionized water is added to this melt and hand mixed until obtaining a homogenous mixture and then poured on a clean glass plate that is maintained at 65 ^{o}C. The glass plate was put into an oven and kept at 85 ^{0}C for 18 hours. The same procedure was repeated with different NCO/OH ratios based on the following calculation:

NCO/OH= $M_{NCO}W_{NCO}$ /[?? $M_{OH}W_{OH}$ +(2/18)W_{H2O}]

M_{NCO} =the number of isocyanate groups in one gram of isocyanate

W_{NCO} = the weight of isocyanate (g)

M_{OH} = the number of hydroxyl groups contained in one gram of polyol

W_{OH} = the weight of polyol (g)

W_{H2O} = the weight of water used

Based on this formulation, the best performing foam was obtained with 1.2 molar ratio of NCO/OH using 1g of polyol and 0.3 g of MDI.

3.5. Chain extended polyurethane synthesis

BABHPP, which is used as phosphorous-containing chain extender in prepolymer preparation, was synthesized according to literature [50]. Typically, a solution of bisphenol-A (22.83 g, 0.10 mol) and phenyl phosphonic dichloride (38.90 g, 0.20 mol) in xylene were stirred at a temperature of 140 ^{o}C for 10 hours. A calculated amount of water (0.2 mol) was then added and the mixture was further stirred at 60 ^{o}C for 4 hours. The product was washed with hot water and white solid product was obtained after filtration. The synthesized BABHPP was used for the preparation of chain extended polyurethanes, namely, PUSiThCE and PUSiAmCE, using PSiTh and PSiAm, respectively, as follows: 1.00 g of polyol and 0.35 g of MDI were mixed by hand mixing for 90 min. and a viscous prepolymer was formed and then 1.00 g of prepolymer was added to the calculated amounts of BABHPP (5.30 g for PSiTh and 4.95 g for PSiAm). The mixtures were allowed to cure at 70 ^{o}C for 6 hrs. in a vacuum oven and rigid foams were obtained.

3.6. Measurements and characterization

Molecular structure of polyols, PSiTh and PSiAm, and polyurethanes, PUSiTh, PUSiAm, PUSiThCE and PU-SiAmCE were characterized by FT-IR. Spectra were recorded on a Shimadzu IR prestige-21 spectrophotometer, which is equipped with ATR having a diamond crystal, in a scanning range of 650-4000 cm^{-1} for 25 scans at a spectral resolution of 4 cm^{-1}. Data were collected and processed using IR solution software. ^{1}H and ^{13}C NMR were used for the characterization of polyols and polyurethanes. Spectra were recorded using SHIMADZU Prestige-21 (200VCE) spectrophotometer operating at 300 MHz and 75 MHz, respectively. For data collection and processing VNMR 6.1 C software was used. Solutions were prepared with deuterated chloroform (CDCl$_3$, 99.8 atom % D) at 15% concentration by volume. The dynamic viscosity of polyols were measured at 25 ^{o}C on SV-10 Series Sine-wave Vibro Viscometer of N&D Company. Hydroxyl numbers of polyols were determined according to ASTM D-1957-86 using acetic anhydride in pyridine and then titrating the acetic acid, which is released due to esterification of hydroxyl groups, with KOH. DSC analysis was used to record phase transition of samples in endothermic process using Mettler Toledo DSC1 200W. 3 mg of samples were weighed in aluminium pans of 40 μL and first cooled down to -90 ^{o}C and then heated to 40 ^{o}C in nitrogen atmosphere with 50 mL/min flow and 10 ^{o}C /min constant heating rate. Thermal degradation of polyols and polyurethanes were investigated in nitrogen atmosphere with 20 mL/min flow and 10 ^{o}C /min heating rate using Netzsch STA 44F1A analyzer. 40-60 mg of samples in 0.3 ml of aluminium crucible were heated from 40 to 600 ^{o}C. Compressive force deflection test for PU foam was performed according to ASTM D1621-16 on a Shimadzu AG-IC 20KN/50KN tensile machine using 56 mm long, 56 mm width, 25.4 mm thick samples at a compression rate of 2.5 mm/min. The flame retardant properties of PU foams were measured by limiting oxygen index (LOI) test in MARES limiting oxygen tester, M LOI 01 following the ASTM D2863- 13 standart procedure using the test specimens cut in dimensions of 100 x 10 x 10 mm (length x width x thickness). X-ray diffractometer (XRD-Rigaku D/MAX 2000) with Cu-K radiation was used to investigate the existence of crystalline and amorphous phases of polyurethanes.

4. Conclusion

Two novel biobased polyols were synthesized by silylation of epoxidized soybean oil through epoxy ring opening reaction with alkoxy silanes. FTIR, ^{1}H NMR and ^{13}C NMR spectra confirmed polyol formation. Polyurethanes, PUSiTh and PUSiAm, prepared from these polyols exhibited flame retardant properties with LOI values of 23.6% and 22.8%, respectively, as a result of the incorporation of silanol groups into the polymer structure. Chain extended-polyurethanes, PUSiThCE and PUSiAmCE, prepared by using BABHPP as the extender showed further flame retardancy with LOI values of 26.3% and 25.6%. Addition of phosphorous into the polymer structure enhanced the LOI value by 11.4% and 12.36%.

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