A study on thermal stability of glycidylsiloxane resins cured with aliphatic amines

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DOI: dx.doi.org/10.14314/polimery.2015.448

Abstract: Oligomeric glycidylsiloxanes are promising components of hybrid amino-epoxy-siloxane coatings with improved properties. The thermal stability of amine-cured glycidylsiloxane resins were studied by means of thermogravimetric analysis. Four samples of glycidylsiloxane resin, with 18 to 30 glycidyl groups per molecule and molar masses from 5 to 10.5 kg/mol, were cured at 140 °C with triethylenetetramine (TETA), isophorone diamine (IDA) and a polyamide (PF). The onset temperatures of degradation, residual masses and heat effects were measured. Maximal degradation rates were registered at temperatures above 400 °C. Infrared spectra of the residues indicate that the least stable bonds are Si-C, C-H and C-N. A second degradation step takes place above 700 °C resulting in disperse silica.

Keywords: glycidylsiloxane resins, curing, thermal oxidative destruction.

Badanie stabilności termicznej żywic glicydylosiloksanowych utwardzanych za pomocą amin alifatycznych

Streszczenie: Zbadano proces termicznego rozkładu powłok z żywic glicydylosiloksanowych utwardzonych przy użyciu trietylenotetraminy (TETA), izoforonodiaminy (IDA) oraz poliamidu (PF). Wytworzone powłoki lakierowe wykazywały odporność na działanie temperatury do 300 °C. W celu doboru optymalnego składu żywicy ocenie poddano próbki o różnej zawartości grup glicydylowych, różnym ciężarze cząsteczkowym i różnym udziale grup siloksanowych. Metodą termograwimetrii wyznaczono temperaturę rozkładu (początkową, maksymalną i końcową), efekty cieplne i całkowitą zmianę masy. Metodą spektrometrii w podczerwieni zidentyfikowano rodzaj produktów powstających w wyniku termodestrukcji.

Słowa kluczowe: żywice glicydylosiloksanowe, utwardzanie, rozkład termooksydacyjny.

Silicoorganic polymers containing silicon atoms in main chains are known to form high quality organic coatings when cured using appropriate hardeners. The most common silicone polymers are polyorganosiloxanes, which may also be modified with other polymers [1—4]. Polyorganosiloxanes are obtained via controlled hydrolysis of alkyl or arylchlorosilanes. They are highly soluble in aromatic and halogenated hydrocarbons, esters and ketones. Modification of polyorganosiloxanes usually leads to a decrease of their thermal stability. The most often used modifiers are various resins (phthalic, acrylic, urea-formaldehyde, melamine-formaldehyde and epoxy), as well as cellulose esters, resin *etc*. [5—7]. The physicochemical properties of cured glycidylsiloxane resins are dependent on both the molecular structure of the oligomer chains and active group location. Application of different hardener types and hardener contents, as well as different curing schedules, results in different properties of the cured polymers.

The composition of silicone-acrylic resins with phthalic resin from soybean oil results in coatings with high gloss and water resistance [8]. Similar coatings were obtained using a composition of silicone resin copolymerized with 4,4′-diaminediphenylmethane, phthalic anhydride and epoxy resin [9—11]. Curing of the composition and formation of the coating consists in the formation of interpenetrating polymer networks [12, 13]. Silicone-epoxy resins are readily co-cured with silicone-amine and silicone-acrylic ones, especially under UV-irradiation [14, 15]. Silicone resins modified with acrylic monomers and isocyanates, as well as silicone resins containing terminal vinyl groups able to cure with nitrile compounds, are interesting materials [16—18].

Branched resins may be obtained via the polymerization of methacrylic monomers linked with silsesquioxanes [19]. Highly branched phthalic-silicone resins were obtained via a multistep synthesis [20, 21]. Polyether-methylsilicone triblock copolymers proved to form

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coatings with good protective and processing properties [22, 23]. Two-step curing of epoxy resin (at first by an aminosilicone compound and secondly by silicone prepolymer) results in a highly crosslinked coating with decreased combustibility [24—26]. Epoxy-silicone resins may also be cured by means of butyltitanates [27]. Coatings with good protective properties and decreased combustibility may be obtained using a composition of cycloaliphatic diphenylepoxy resin cured with triethylenetetramine and the addition of glycidoxypropyltrimethoxysilane (GPTMS) [28, 29]. Silicone resins may be applied for the modification of non-aqueous acrylic dispersions [30, 31]. The thermal resistance of polyurethane coatings may be increased by the addition of epoxy resins containing glycidoxypropyltrimethoxysilane and polyamines [32, 33]. The adition of 5 to 10 wt % of polyorganosiloxane to film-forming resins results in an improvement in the thermal and atmospheric stability, as well as conferring water resistance properties [6, 7, 34—36].

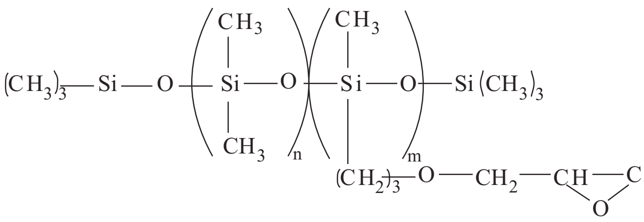
Side groups on the polyorganosiloxane chain define the solubility of the polymer in organic solvents, bending strength and thermal stability. Unmodified polyorganosiloxanes form crosslinked structures at temperatures of 200—250 °C. Resistance against thermal oxidative destruction is very important. Generally, siloxane coatings maintain gloss and resistance to yellowing and cracking under oxidation at increased temperatures. Inflammable siloxane coatings are also known [2, 4, 37—39]. In the case where added resins do not react with polyorganosiloxanes, the obtained coatings have rather ordinary protective properties. Phthalic resins react with polyorganosiloxanes resulting in coatings with good adhesion to building materials. Varnish materials may also contain polymethylphenoxysiloxane modified with glyphthalic or polybuthylmethacrylate resin, a triple copolymer of buthylmethacrylate, buthylacrylate and acrylic acid, as well as hardener [1, 4, 40—42].

The present study concerns the thermal resistance of glycidylsiloxane oligomers cured with aliphatic and cycloaliphatic amines. The thermal properties of the resins with different contents of epoxy groups were determined. The probable reactions occurring under thermal degradation were supported by FT-IR spectroscopy.

EXPERIMENTAL PART

Materials and preparation of resin samples

Four samples of glycidylsiloxane oligomers with the general formula (I) have been synthesized via the addition of allyl glycidyl ether with oligo(methylhydro)siloxanes [43]. Tris(divinyltetramethyldisiloxane)diplatinum(0) (Aldrich) was used as hydrosilylation catalyst. The content of glycidyl groups in the obtained siloxane copolymers was determined by means of ^{13}C and ^{1}H NMR spectra recorded on a Varian Gemini 300 VT spectrometer. Number average molecular weights were determined by means of GPC analysis (Waters Alliance 2695). The obtained numerical characteristics are presented in Table 1.



$$(CH_3)_3-Si-O-\left(\begin{array}{c}CH_3\\ |\\ Si-O\\ |\\ CH_3\end{array}\right)_n\left(\begin{array}{c}CH_3\\ |\\ Si-O\\ |\\ (CH_2)_3-O-CH_2-\underset{\diagdown O \diagup}{CH-CH_2}\end{array}\right)_m-Si(CH_3)_3$$

(I)

T a b l e 1. Properties of the studied glycidylsiloxane resins

Resin type	*n*	*m*	Average molecular weight	Epoxy group content wt %	Silicone content wt %
A	82	18	9360	8.27	3.28
B	50	25	8210	13.10	3.81
C	70	30	10560	12.22	3.70
D	0	28	5030	23.91	6.00

The curing agents used in the study were triethylenetetramine (TETA) (Sigma), technical-grade isophorone diamine (IDA) and polyamide (PF) (Organika S.A. Sarzyna, Poland). The silicon dioxide used in the study was pyrogenic silica (Aerosil R-974) (Degussa AG, Germany).

Stoichiometric quantities of amine hardeners were calculated, taking into account their amine numbers and epoxy number of the resins under the assumption that both primary and secondary amine groups are active in the reaction with glycidyl groups [44]. Besides the calculated content, TETA hardener was also applied in sub-stoichiometric and super-stoichiometric quantities. Because amine hardeners and the glycidylsiloxane oligomers proved to be immiscible, thorough pre-mixing of the reactive components (for 5 min) was applied. An increased temperature (140 °C) and shorter time (20 min) were also applied in order to prevent phase separation when curing.

Methods of testing

— Both thermal and thermogravimetric analyses were carried out under an air atmosphere with a heating rate of 5 °C/min using a Derivatograph Q1500D (MOM, Hungary). Aluminum oxide was applied as an inert filler in the ceramic crucible. Benzoic acid was used as a reference material for heat effect measurements.

— Infrared spectra of the cured glycidylsiloxane resin samples were recorded by means of a Bruker Alpha-P spectrometer in the ATR mode on a diamond window with 64 scans using the Opus 6.5 software.

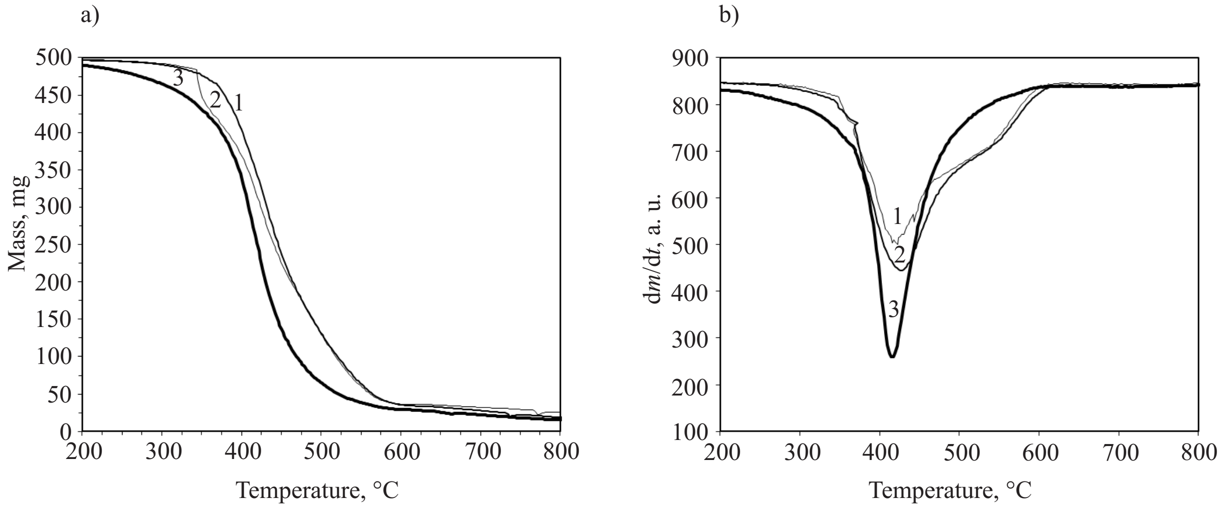


Fig. 1. Exemplary: a) TGA, b) DTG curves of glycidylsiloxane resin of type B cured with TETA at: 1 — 5.77 wt %, 2 — 13.2 wt %, 3 — 37.89 wt %

RESULTS AND DISCUSSION

The obtained thermogravimetric curves are presented in Fig. 1a. Onset decomposition temperatures and temperatures of maximal degradation rate were estimated from differential gravimetric curves (Fig. 1b) and the parameters are listed in Tables 2 and 3.

The presented data clearly indicate that the thermal resistance of the studied glycidylsiloxane resins is dependent on both resin type and hardener. The resins of types A, B and C cured with TETA possess good thermal resistance. Thermal decomposition begins to occur at temperatures above 300 °C and the temperature of the maximal decomposition rate is equal to approximately 410—420 °C (Fig. 1b). The resin of type D cured with TETA has an inferior thermal resistance — the initial decomposition temperature is equal to approximately 200 °C and the temperature of maximal decomposition rate is equal

Table 2. Characteristic temperatures and heat effect of the first step of thermal degradation of the glycidylsiloxane resins

Resin type and hardener	Hardener content wt %	T_{ini} °C	T_{max} °C	T_{end} °C	Heat effect kJ/g	Residue at T_{end} mass %
A-TETA	7.87	333	426	500	0.35	22.2
	13.7	346	419	460	0.18	35.9
	26.05	347	420	453	0.15	32.3
B-TETA	5.8	309	410	521	0.58	19.1
	13.2	294	413	474	0.28	37.4
	37.9	369	422	462	0.13	22.7
C-TETA	9.8	315	416	530	0.32	21.5
	14.4	283	412	493	0.38	24.6
	41.3	323	415	453	0.07	21.2
D-TETA	6.32	204	363	454	0.21	42.9
	14.6	201	400	446	0.30	44.0
	27.4	200	383	434	0.26	42.2
A-IDA	21.5	337	404	451	0.24	22.1
C-IDA	33.1	336	411	470	0.29	12.4
D-IDA	24.7	200	380	452	0.61	38.4
A-PF	21.9	250	400	472	0.32	30.3
B-PF	25.8	238	403	464	0.29	32.4
C-PF	35.7	262	394	465	0.10	38.0
D-PF	23.4	226	390	476	0.69	31.2

Table 3. Characteristic temperatures and heat effect of the second step of thermal degradation of the glycidylsiloxane resins

Resin type and hardener	Hardener content wt %	T_{ini}, °C	T_{max} °C	T_{end} °C	Heat effect kJ/g	Residue at 1000 °C mass %
A-TETA	7.87	529	704	833	1.51	1.9
	13.7	532	715	836	1.52	3.0
	26.05	536	721	835	1.07	1.8
B-TETA	5.8	555	751	862	1.45	4.7
	13.2	552	747	852	1.51	3.2
	37.9	551	773	942	1.26	2.3
C-TETA	9.8	573	705	777	1.02	3.8
	14.4	560	700	800	1.02	2.3
	41.3	559	745	805	0.49	2.5
D-TETA	6.32	551	756	809	0.96	25.7
	14.6	521	779	936	2.39	25.3
	27.4	518	830	931	2.28	21.6
A-IDA	21.5	514	712	820	0.63	4.6
C-IDA	33.1	495	592	739	0.43	3.2
D-IDA	24.7	503	770	885	2.10	21.4
A-PF	21.9	510	640	775	1.03	4.4
B-PF	25.8	506	644	729	1.25	3.8
C-PF	35.7	528	633	698	0.61	4.2
D-PF	23.4	487	807	940	2.28	17.9

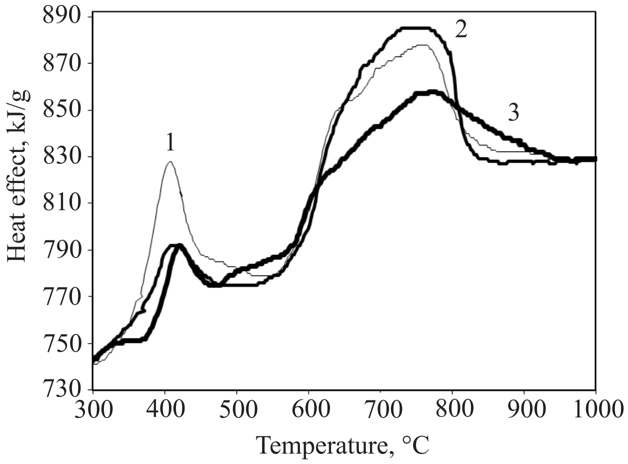


Fig. 2. Exemplary DTA curves of glycidylsiloxane resin of type B cured with TETA at: 1 — 5.77 wt %, 2 — 13.2 wt %, 3 — 37.89 wt %

to 400 °C (Table 2). The glycidylsiloxane resin of type B cured with the IDA hardener decomposed rapidly (at a temperature of about 200 °C), resulting in a small explosion.

Thermal analysis curves proved to have two maxima (Fig. 2.) clearly indicating that the thermal degradation of the studied glycidylsiloxane resins occurs as a two-step process. The obtained values of characteristic temperatures and heat effects for the first degradation step are presented in Table 2.

Generally, the first degradation step is characterized by a moderate heat effect and results in a residue mass equal to 20-40 mass %. One can see a regularity that increased hardener content leads to a decreased heat effect of thermal degradation. The second degradation step begins at temperatures of about 520 °C for all the studied resins. The heat effect of the second step is larger compared to that of the first step. Probably, it is the second step that results in oxidation and complete chemical decomposition of the resin.

Infrared spectroscopy of the residues has been applied in order to determine the chemical products arising from both degradation steps. Figures 3 to 7 show spectra of the samples heated to the specified temperatures. The infrared spectrum of dispersed silica is presented for reference purposes.

The interpretation of the registered spectral changes was made using literature data [45]. The characteristic wave numbers ascribed to chemical groups occurring in the initial and degraded glycidylsiloxane resins are collected in Tables 4 and 5.

Spectra of glycidyl siloxane resins of all the studied types contain strong signals from methylene and methyl groups linked with silicon atoms, as well as from siloxane groups. Spectra of the cured resins also contain strong signals of secondary and tertiary nitrogen atoms and ethylene groups from the amine hardener. The spectra remain unchanged up to the temperature of the first degradation step (411, 451, 419 and 409 °C for the resins of type

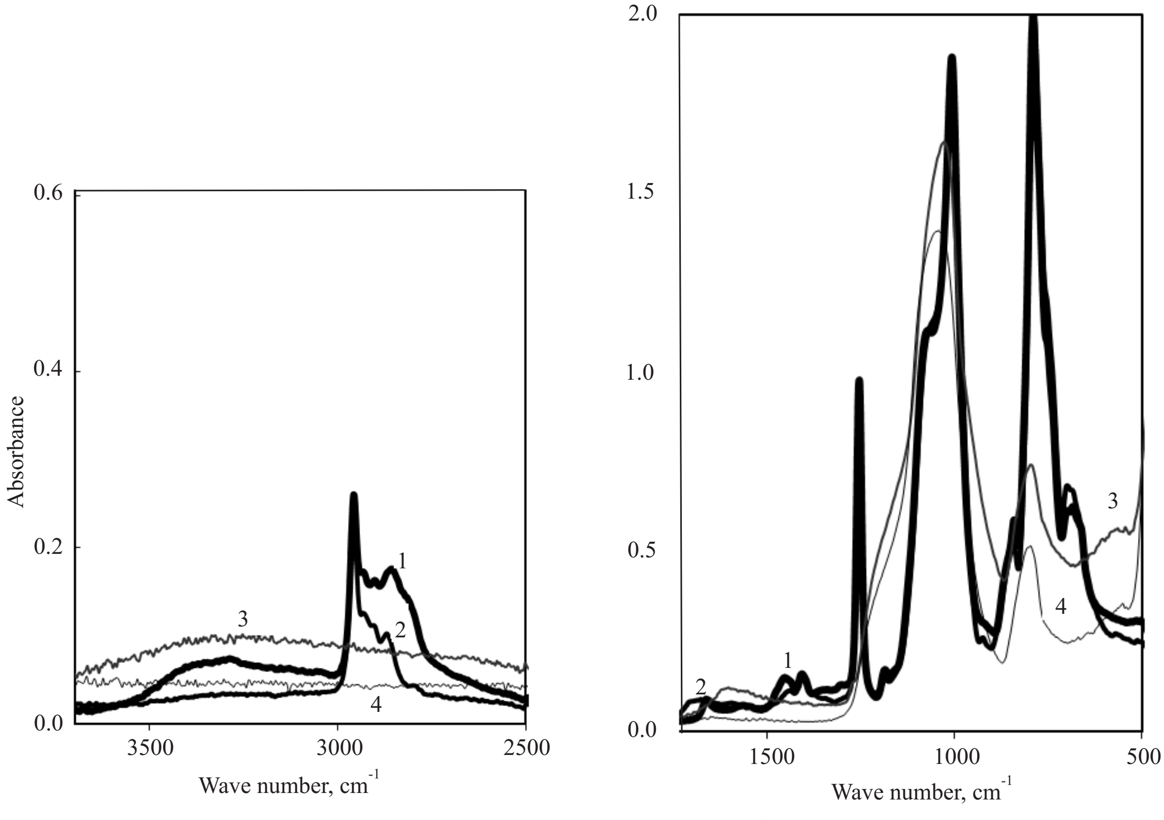


Fig. 3. FT-IR spectra of glycidyl siloxane resin of type A cured with TETA at 13.7 wt %; heating temperatures: 1 — 140 °C (as cured), 2 — 411 °C (first degradation step), 3 — 733 °C (second degradation step), 4 — 900 °C (full decomposition)

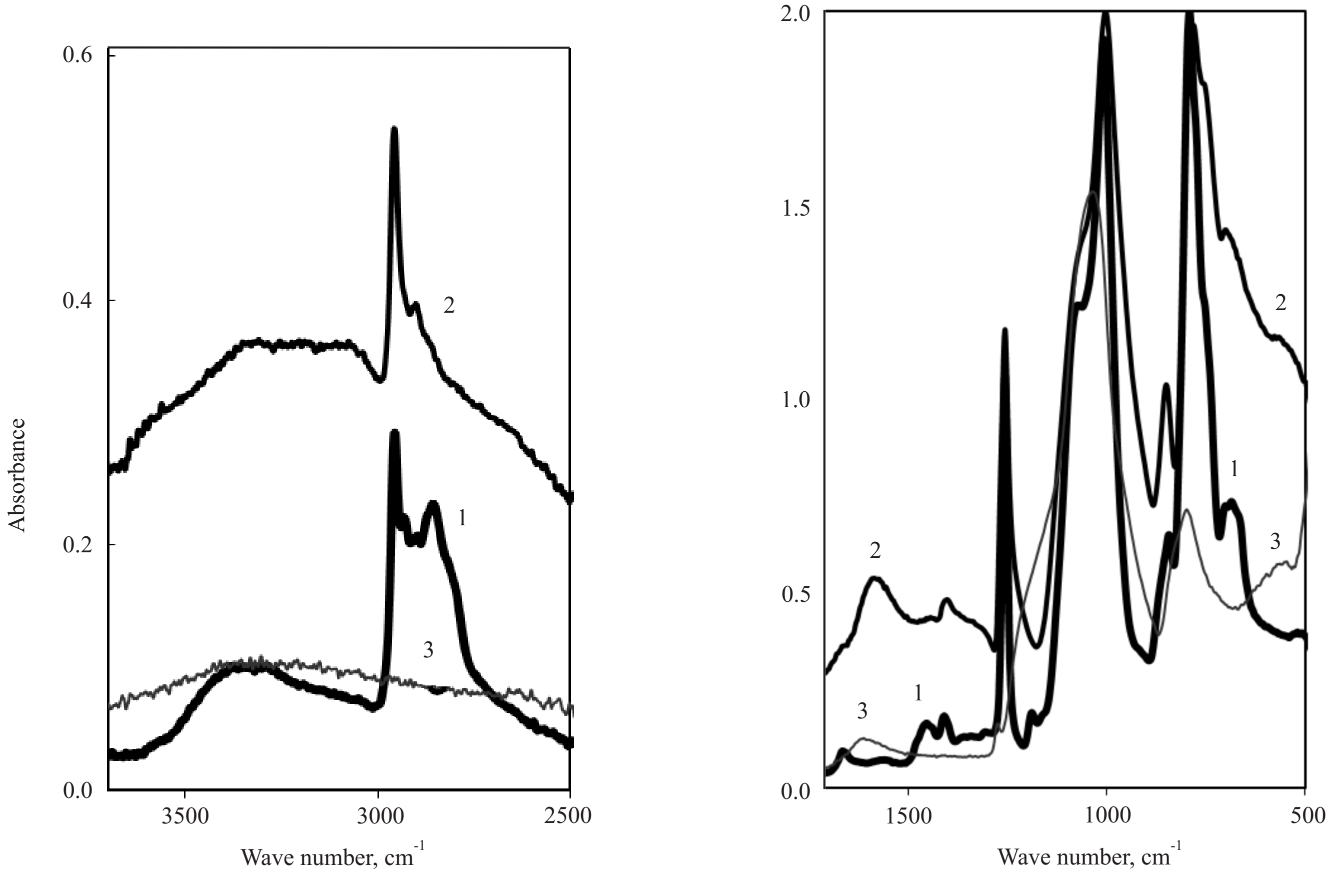


Fig. 4. FT-IR spectra of glycidylsiloxane resin of type B cured with TETA at 13.2 wt %; heating temperatures: 1 — 140 °C (as cured), 2 — 451 °C (first degradation step), 3 — 719 °C (second degradation step)

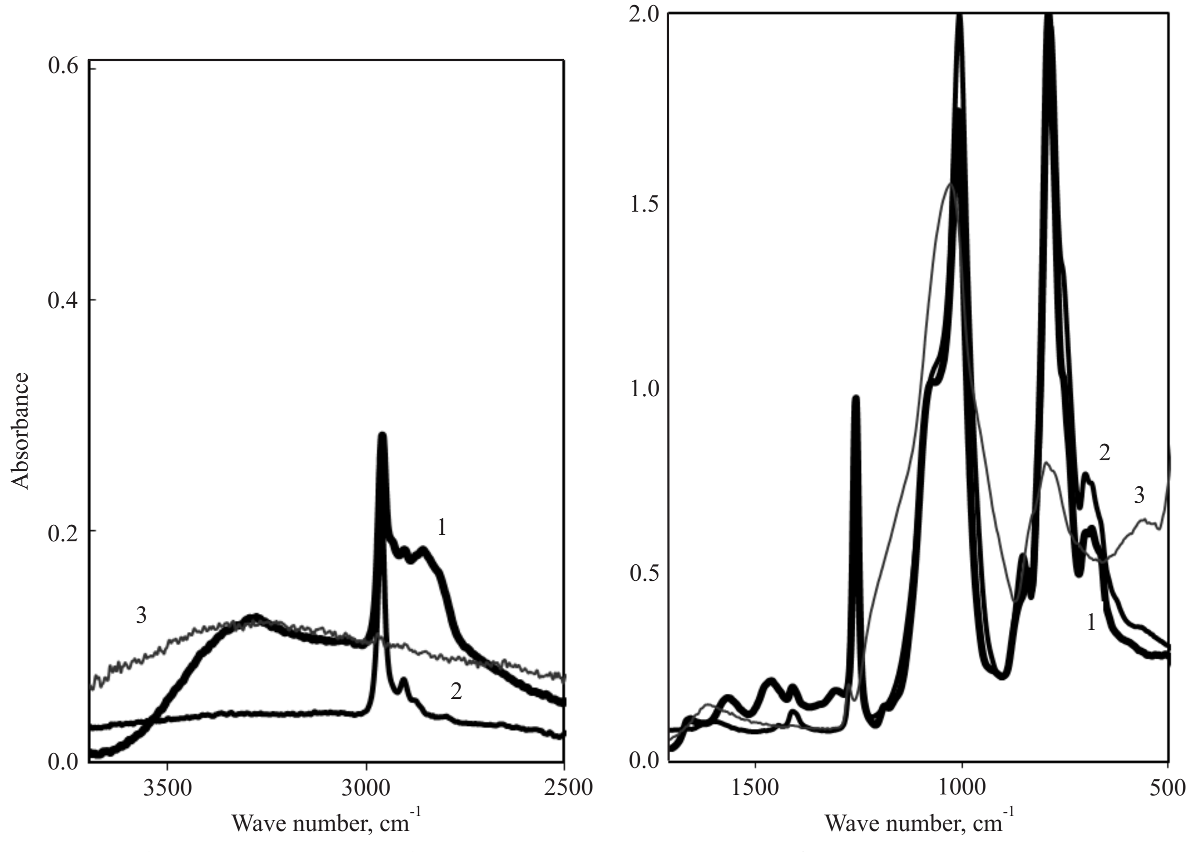


Fig. 5. FT-IR spectra of glycidylsiloxane resin of type C cured with TETA at 14.4 wt %; heating temperatures: 1 — 140 °C (as cured), 2 — 419 °C (first degradation step), 3 — 700 °C (second degradation step)

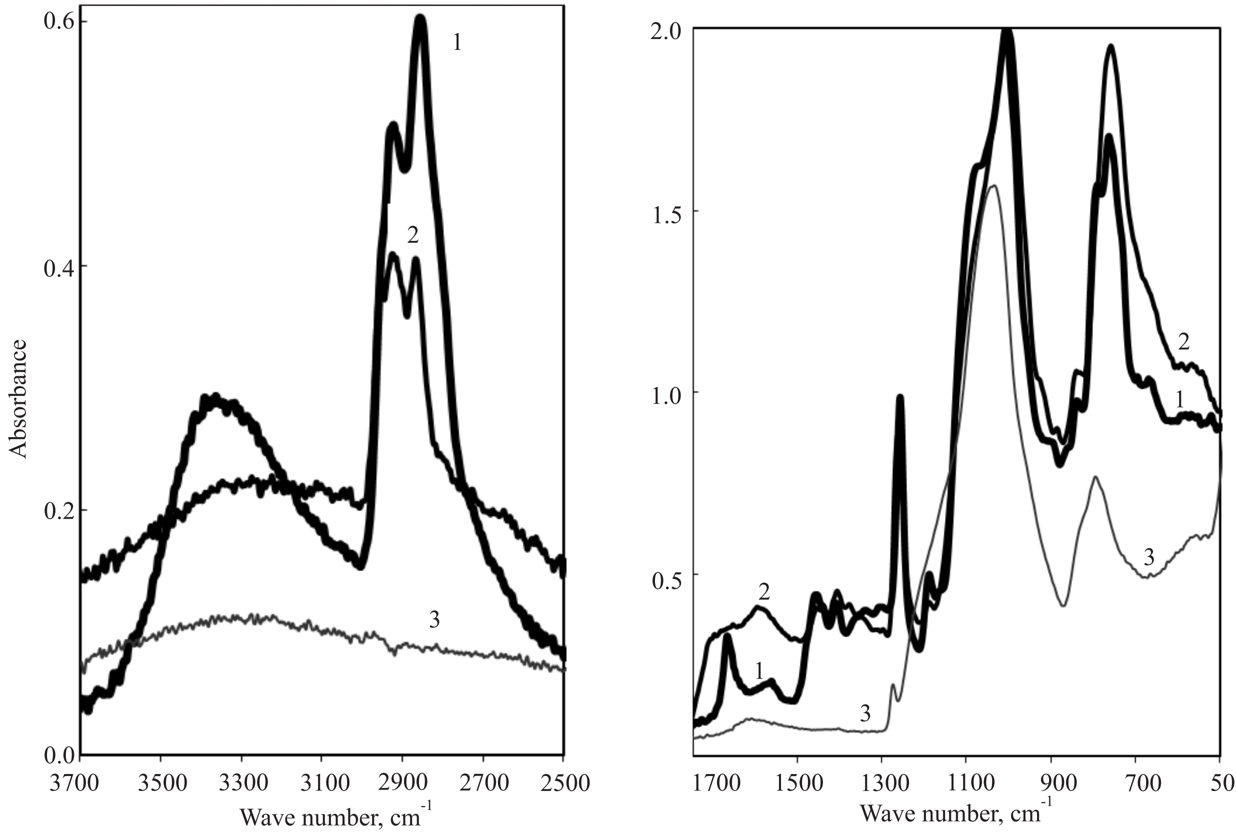


Fig. 6. FT-IR spectra of glycidylsiloxane resin of type D cured with TETA at 14.6 wt %; heating temperatures: 1 — 140 °C (as cured), 2 — 409 °C (first degradation step), 3 — 732 °C (second degradation step)

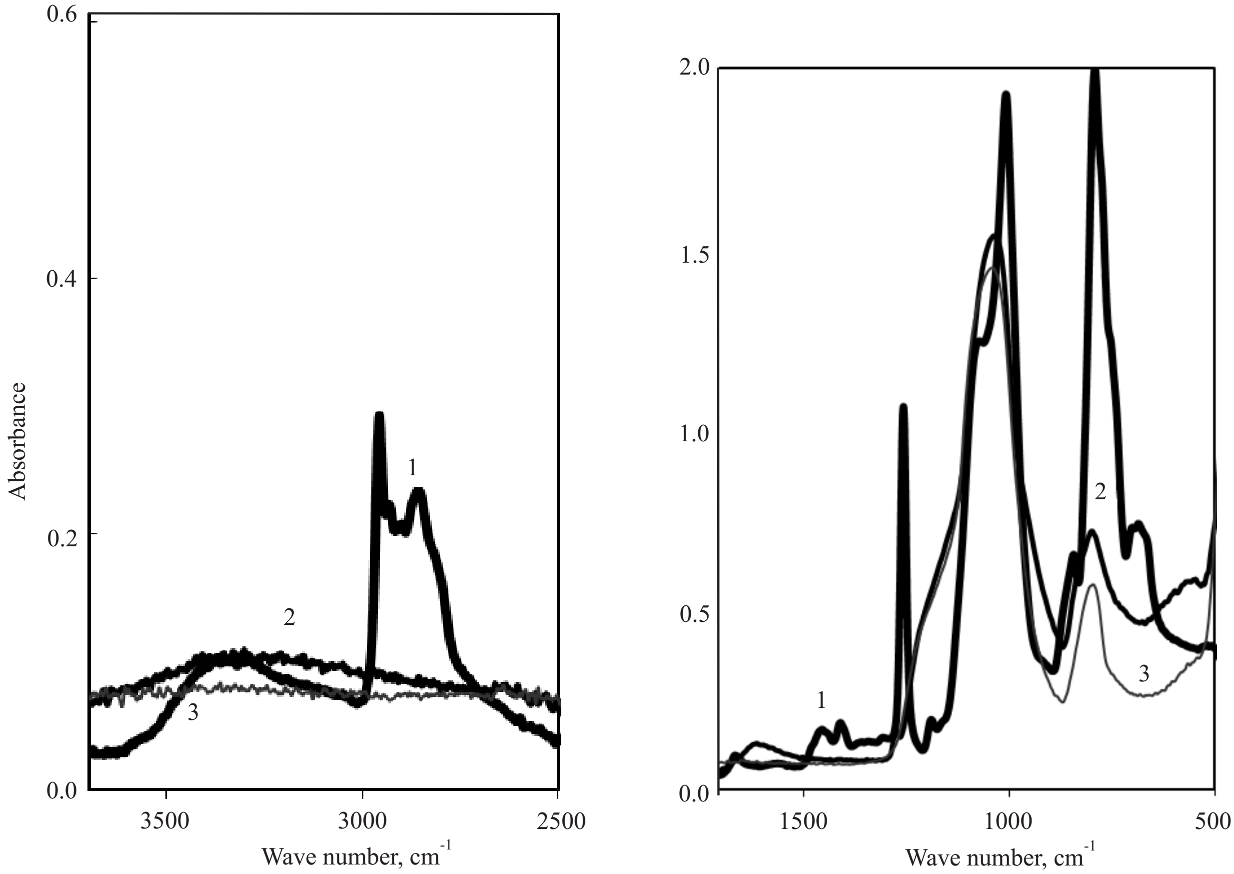


Fig. 7. FT-IR spectra of glycidylsiloxane resin of type B cured with TETA at 13.2 wt %; heating temperatures: 1 — 140 °C (as cured), 2 — 719 °C (second degradation step); curve 3 is disperse silica heated to 900 °C

T a b l e 4. Specific chemical groups and characteristic wave numbers (cm^{-1}) of FT-IR bands registered for the initial, cured and degraded glycidylsiloxane resins of types A and B

Specific group	Glycidylsiloxane resin type A				Glycidylsiloxane resin type B		
	20 °C	411 °C	733 °C	965 °C	20 °C	451 °C	719 °C
Si-CH$_2$, Si-CH$_3$	842 lo	845 lo	-	-	843 lo	850 lo	-
Si-CH$_2$, Si-CH$_3$	1257 hi	1257 hi	-	-	1257 hi	1257 hi	-
Si-CH$_3$	700 lo 685 lo	700 lo 685lo	-	-	701 lo 685 lo	700 -	-
Si-CH$_3$	791 hi	789 hi	-	-	791 hi	781 hi	-
NH-	2960 lo	2961 lo	-	-	2960 hi	2960 hi	-
CH$_2$-N, NH-	2859 lo	2873 lo	-	-	2860 lo	-	-
C-C	1009 hi	1009 hi	-	-	1008 hi	1003 hi	-
NH-	3340 lo	3300 lo	3300 lo	-	3280 lo	3312 lo	-
NH-	1667lo 1570 lo	1681 lo 1599 lo	1607 lo	-	1667 lo 1562 lo	1597 lo hi!	
NH-	1457 lo 1410 lo	1441 lo 1410 lo		-	1455 lo 1411 lo	1455 lo 1403 lo	
NH -	1188 lo	1188 lo	-	-	1189 lo	-	-
Si-O	791 hi	791 hi	796 hi	796 hi	791 hi	781 hi	798 hi
Si-O-C, Si-O-Si	1056 lo	1056 lo	1028 hi	1045 hi	1075 lo	1075 lo	1036 hi
Si-O	448 hi	448 hi	448 hi	448 hi	430 hi	430 hi	382 hi

T a b l e 5. Specific chemical groups and characteristic wave numbers (cm^{-1}) of FT-IR bands registered for the initial, cured and degraded glycidylsiloxane resins of types C and D

Specific group	Glycidylsiloxane resin type C			Glycidylsiloxane resin type D		
	20 °C	419 °C	701 °C	20 °C	409 °C	732 °C
Si-CH$_2$, Si-CH$_3$	842 lo	852 lo	-	838 lo	839 lo	-
Si-CH$_2$, Si-CH$_3$	1257 hi	1257 hi	-	1257 hi	1259 hi	-
Si-CH$_3$	699 lo 685 lo	701 lo 685 lo	-	695 lo 669 lo	- -	- -
Si-CH$_3$	790 hi	785 hi	-	791 lo 763 hi	- 759 hi	795 -
NH-	2960 hi	2960 hi	-	2925 lo	2926 lo	-
CH$_2$-N, NH-	2858 lo 2906 lo	- 2906 lo	- -	2859 hi	2870 low	-
C-C	1009 hi	1006 hi	-	1007 hi	1002 hi	-
NH-	3278 lo	-	-	-		
NH-	1658 lo 1569 lo	1712 lo 1604 lo	1616 lo -	1697 lo 1596 lo	1697 lo 1596 lo	1609 lo -
NH-	1461 lo 411 lo	1444 lo 1411 lo	-	1457 lo 1409 lo	1457 lo 1409 lo	-
NH -	1187 lo	-	-	1188 lo	1189 lo	-
Si-O	790 hi	785 hi	796 hi	791 lo 763 hi	- 759 hi	795 hi -
Si-O, Si-O-C Si-O-Si	1076 lo	1076 lo	1028 hi	1077 lo	-	1039 hi
Si-O-	425 lo 378 hi	425 lo 378 hi	425 hi	402 hi	402 hi	431 hi

A, B, C and D, respectively). One can infer that the mentioned temperatures indicate practical thermal resistance of the resins in question. Thermal degradation of the resins begins to occur above the mentioned temperatures. Probably, the decomposition process starts with Si-C, C-H and C-N chemical bonds known to possess rather low energies. Residues of the mentioned chemical bonds are registered at temperatures slightly above 700 °C. On the other hand, siloxane bonds are much stronger and the corresponding spectral bands remain present up to temperatures of about 900 °C.

CONCLUSIONS

Four samples of glycidylsiloxane resin were cured with technical-grade amine hardeners applied thorough pre-mixing and short curing times in order to prevent phase separation when curing. FT-IR spectra suggest that all the studied resins were successfully cured, resulting in polymers of similar structures. TGA data indicate that the cured resins possess rather similar thermal stabilities. More stable resins are cured with triethylenetetramine having temperatures of maximal degradation rate in the range from 410 to 426 °C, except for low-molecular weight resin of type D. The resin of type B cured with the IDA hardener decomposed rapidly (at a temperature of about 200 °C) resulting in a small explosion. Heating to temperatures above 700 °C results in full thermal degradation and the formation of dispersed silica.

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Received 4 VII 2014.