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Thermal properties of phthalonitrile functional polybenzoxazines

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Abstract

Phthalonitrile functional polybenzoxazines show high thermal stability with temperature at 5% weight loss ($T_{5\%}$) up to 450°C for monofunctional benzoxazine-based polymers, and up to 550°C for polymers from the bifunctional precursors. High char yield up to 80% by weight is obtained by thermogravimetric analysis in an inert atmosphere at 800°C. Char yield up to 70% by weight at 600°C is achieved in air with $T_{5\%}$ in the 380–420°C range. Differential scanning calorimetry (DSC) is used to determine curing conditions. These resins do not require ultrahigh curing temperature as it is typical for the other phthalonitrile functional prepolymers and 250°C is used as a maximum post-cure temperature to achieve desired properties. Dynamic mechanical analysis (DMA) reveals unusually broad dependence of loss modulus vs. temperature with the maximum at 300°C for polybenzoxazines from bifunctional precursors and 278°C for polymer from monofunctional precursors. Additionally, these materials exhibit low flammability. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Polybenzoxazine; Phthalonitrile; Glass-transition temperature; Thermal property; Flammability

1. Introduction

Polymers with easy processability, good mechanical properties, and high thermal stability are in increasing demand as matrix materials for advanced composites [1]. It has long been recognized that, in order to achieve heat resistance, the presence of aromatic and heterocyclic ring structures in the polymer main chain structure is necessary. However, it is difficult to fully utilize those highly stable structural units in polymers, because they tend to be brittle, insoluble, and infusible. One approach is to utilize prepolymers end-capped with reactive alicyclic rings, which polymerize by addition reaction [2,3]. Other approaches include making resins with acetylene functional groups, because oligomers and polymers containing acetylenic groups can be polymerized into three-dimensional void-free networks under moderate conditions, and these polymers show solvent resistance, moisture resistance, and excellent thermo-oxidative stability [4–14].

High-performance phthalonitrile-terminated polymers have also been developed and used for many applications [15–18]. Phthalonitrile-based prepolymers with low molecular weight are stable at room temperature and the prepolymers can be processed to form void-free cross-linked polymers by heating in the presence of thermally stable aromatic amines [15–18].

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Imide-containing phthalonitrile resins exhibit char yield of 60% by weight in an inert atmosphere when cured at 315°C for 16 h and further post-cured at 375°C with added 1% by weight of hexakis(4-aminophenoxy)cyclotriphophazene catalyst. Char yield at 600°C in air was found to be 20% by weight, while $T_{5\%}$ remained unchanged [14]. It has also been reported that neat polymerization of phthalonitrile resins is difficult even under extreme thermal conditions, because these monomers do not contain an active hydrogen [17]. Neat polymerization of bisphenol-linked phthalonitrile monomers required several days of continuous heating at 290°C, before viscosity increase is detected. The slow rate of polymerization can be attributed to the rigidity of the linking sites, which reduces the mobility of the reaction sites or, more likely, to the absence of initiating agents [17]. Aromatic diamines are considered to be suitable candidates as curing agents of phthalonitrile polymerization. They generate an active intermediate, which reacts rapidly with the excess of phthalonitrile functionalities. No volatiles are generated from this reaction. They are usually compatible with the monomer and can be easily molecularly dispersed [17]. Nevertheless, a bisphenol-linked phthalonitrile resin with 10% by weight of diamine curing agent was polymerized at 280°C for an extended period and temperature at 10% weight loss ($T_{10\%}$) was in the range of 460 to 480°C in an inert atmosphere and 440 to 470°C in air [17]. Dynamic mechanical analysis of phthalonitrile-based resins showed that the largest modulus change with a viscoelastic transition to the rubbery state occurred between 200–360°C [19]. However, the samples further post-cured at 375°C did not exhibit a T_g, and they appear to retain about 73% of their initial modulus [19]. Bisphenol-linked phthalonitrile resins, when cured at 316°C for 16 h, did not show a sharp glass-transition temperature in the DSC thermograms, but rather a broad viscoelastic transition to the rubbery state. When the samples were further post-cured at 375°C for 24 h, the polymer did not display a T_g. It was proposed that polymer became highly cross-linked with little molecular mobility within the backbone at elevated temperatures [15]. It has been recently reported, that phthalonitrile resin-based composites for an aerospace application were autoclave cured, but additional post-cure at 375°C for 8 h was required to maximize mechanical properties and thermal stability. The char yield of the post-cured sample improved from 60% by weight to 70% by weight [20].

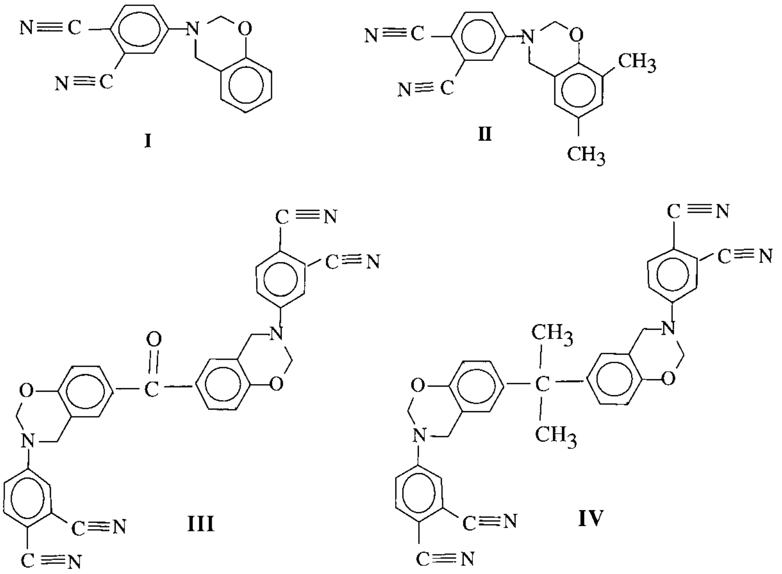
Polybenzoxazines have been investigated in our laboratory for several years [21]. Since these resins polymerize via ring-opening polymerization, no by-products are released during polymerization. In addition, excellent processability and low water absorption make the benzoxazine resins ideally suited as matrices for high performance composite applications. Despite their usual thermal stability, the side functional groups R (phenyl) of the Mannich bridge, $-CH_2-NR-CH_2-$, were found to be the weakest points of the cross-link networks. Therefore 'end-capping' of these functionalities by another polymerizable group, such as phthalonitrile was expected to stabilize the Mannich bridge, which would further improve the thermal stability of polybenzoxazines. This concept was successfully used for development of high performance acetylene functional polybenzoxazines [22]. It is also expected that side functionality, phthalonitrile, will contribute to the cross-link network formation by its own polymerization. It has been reported elsewhere that only a fraction of the nitrile functionalities reacts during polymerization of phthalonitrile functional polybenzoxazines [23]. In this paper, it is intended to investigate how the further reactions of remaining nitriles at higher temperature affect char formation of these materials. It is also intended to study general thermal characteristics of these resins, such as curing conditions and glass transition temperature.

2. Experimental

Synthesis, characterization and proposed polymerization mechanism of phthalonitrile functional benzoxazines are discussed in detail elsewhere [23]. The monomers shown in Scheme 1 have been investigated.

2.1. Thermal analysis

The thermal stability of polybenzoxazines in isothermal and dynamic modes was investigated by thermogravimetric analysis (TGA) performed on a TA Instruments thermogravimetric analyzer, high-resolution TGA 2950, which is equipped with an evolved gases analysis (EGA) furnace. The evolved gases were collected in the gas cell of the TGAIFT-IR



Scheme 1. Phthalonitrile functional benzoxazine monomers.

interface and analyzed on the FTS-60A Bio-Rad infrared spectrometer with a resolution of 8 cm^{-1}. The temperature of the transfer line and the gas cell was kept constant at 300°C for all experiments. Nitrogen was used as a purge gas for all testing. The char yield of the polybenzoxazines was determined as the solid residue which remained at 800°C under nitrogen purge and at 600°C in air. A heating rate of 20°C/min was used for all tests. Differential scanning calorimetry (DSC) was performed on TA Instruments high-pressure DSC 2910 with a heating rate of 10°C/min and under pressure of 2.75 MPa using nitrogen purge and an empty aluminum pan as a reference. The high-pressure cell was used since phthalonitrile functional benzoxazines polymerize at high temperatures and this process can overlap with degradation.

2.2. Dynamic mechanical analysis (DMA)

The specimen for dynamic mechanical analysis was prepared by thermal polymerization of degassed monomers in the specifically designed mold. Mold consists of a U-shaped silicon rubber spacer placed between two glass plates which were treated with a silicone-based mold-release agent. Mold is placed vertically in a vacuum oven and 4 g of monomer was degassed for several hours at 160°C. Next, the mold was placed into the air-circulating oven and the monomers were polymerized by heating up to 220°C and post-cured at 250°C for 6 h. The void-free specimens with dimensions of ≈48mm×12mm×3 mm were then sanded to obtain a smooth surface. Dynamic mechanical spectra were recorded with Rheometrics dynamic mechanical spectrometer (RMS-800) equipped with a 200–2000 g cm dual-range, force rebalance transducer. Specimen were tested in rectangular torsion fixture. A maximum strain of 0.1% was applied sinusoidally during each temperature sweep at a frequency of 1 Hz. Strain sweep experiment was performed to ensure that this strain is within the linear viscoelastic limit. The experiment was performed at a heating rate of 2°C/min from 50 to 300–350°C. Samples were submitted to a thermal soak time of 30 s for each temperature change.

Flammability of the resins was tested in the Federal Aviation Administration (FAA) laboratories on a small quantity of samples in a micro-cone calorimeter.

3. Results and discussion

3.1. Thermal analysis

Non-isothermal DSC thermograms of phthalonitrile-modified bifunctional benzoxazine precursors

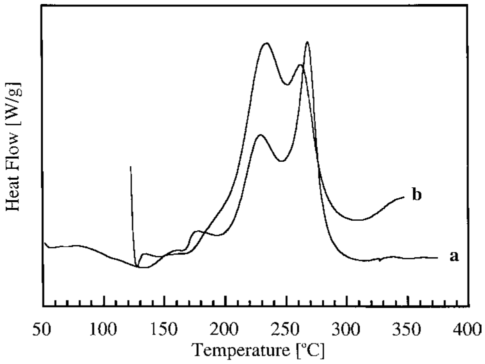


Fig. 1. DSC thermograms of benzoxazines **III** (a) and **IV** (b).

III and **IV** are shown in Fig. 1. DSC analysis of catalyzed and uncatalyzed polymerization of monofunctional precursors **I** and **II** was described previously [23]. It is noticeable, that the maxima of the exothermic peaks are shifted to the lower temperatures for bifunctional precursors when compared with monofunctional phthalonitrile-based benzoxazines as shown in Table 1. Generally, bifunctional benzoxazines-based on unfunctional amines show exothermic peak at lower temperatures than their monofunctional analogs partly due to the higher concentration of phenolic impurities in the bifunctional resins. It has been demonstrated that, for phthalonitrile functional benzoxazines, oxazine ring opening and phthalonitrile addition reaction are closely connected [23]. Consequently, maxima of the exotherms representing polymerization of phthalonitrile for benzoxazines **III** and **IV** are also shifted to lower temperatures. Additionally, when compared with other phthalonitrile resins, phthalonitrile exotherm maxima for shown benzoxazines are shifted to lower temperatures (Table 1) [15] The polymerization temperature of 250°C used for these precursors is significantly lower than the reported temperatures for polymerization of other phthalonitrile prepolymers [15].

Table 1
DSC analysis and curing conditions of phthalonitrile functional benzoxazines

Monomer	$T_{\mathrm{exo(benzox)}}$ (°C)	$T_{\mathrm{exo(nitrile)}}$ (°C)	T_{cure} (°C)	t_{cure} (h)
I	268	285	240	6
II	314	330	280	6
III	234	262	250	6
IV	227	268	240	6

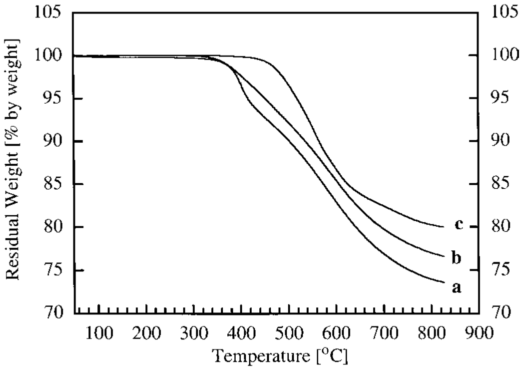


Fig. 2. TGA curves of polybenzoxazines **I** (a), **II** (b) and **III** (c) tested in nitrogen.

TGA curves of polybenzoxazines from the **I**, **II** and **III** monomers polymerized at optimum conditions are shown in Fig. 2. The highest char yields of 77 and 80% by weight were achieved by polybenzoxazines from **I** and **III**, respectively. The temperatures at 5% weight loss ($T_{5\%}$) for these resins were 450 and 550°C, respectively. It is believed that the high char yield of these polybenzoxazines is a result of further thermal polymerization of the nitriles, which remained unreacted during the initial polymerization stage [23]. Fig. 3 displays TGA curves of the same polybenzoxazines, but the tests were performed in air in order to investigate thermo-oxidative stability of these resins. For most of the thermosetting resins, thermooxidation process starts around 500°C and at 600°C

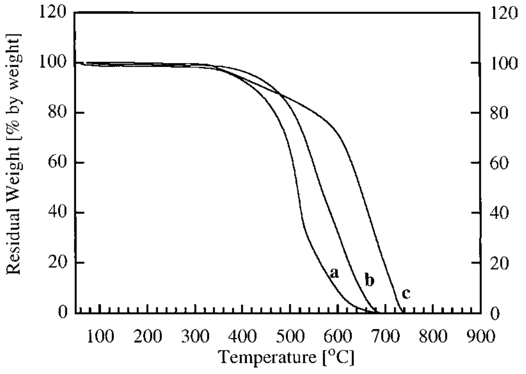


Fig. 3. TGA curves of polybenzoxazine **I** (a), **II** (b) and **III** (c) in air.

Table 2
TGA analysis results of phthalonitrile functional polybenzoxazines and other phthalonitrile functional resins

Benzoxazine	Nitrogen			Air		
	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	Char yield (wt.%) 800°C	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	Char yield (wt.%) 600°C
I	450	560	76	420	440	50
II	414	505	73	378	420	0
III	544	596	80	390	450	75
IV	423	468	68	–	–	–
I+5%$FeCl_3$	415	485	74	–	–	–
I+5%DDE	441	523	76	–	–	–
PH-polyimide [18]	530	550	65	500	510	10
Phthalonitrile [15]+2% diamine	460	500	70	500	500	50

char yield equals zero [24]. Phthalonitrile functional polybenzoxazine **III** exhibits excellent thermo-oxidative stability up to 500°C, and at 600°C it still exhibits significant char yield of 70% by weight. Polybenzoxazines **I** and **II** exhibit $T_{5\%}$, in the temperature range of 380–420°C. As expected, the poorest performance, among all the polymers studied, was observed with polybenzoxazine **II**. This resin does not contain highly cross-linked Mannich-based networks, since the precursor has blocked the ortho position of the benzene ring and the oxazine ring opening polymerization through the meta position probably does not proceed to a high extent. TGA results are summarized in Table 2. Fig. 4 shows TGA curves of polybenzoxazine **I** cured in the presence of 5% by weight of 4,4′-diaminodiphenylether (DDE) and 5% by weight of $FeCl_3$. Both were chosen as catalysts for phthalonitrile functional benzoxazine polymerization. It was discussed in detail previously, that $FeCl_3$ decreased significantly the polymerization temperature of phthalonitrile-based benzoxazines; however, a lower degree of nitrile conversion during polymerization was achieved [23]. As it is obvious from this figure, $T_{5\%}$ and the char yield slightly decreased. Since metal chlorides are also effective catalysts of oxazine ring polymerization, this may be a result of significantly increased content of less thermally stable Mannich base bridges. Interestingly, there is a further degradation process taking place at the temperature above 800°C, which is in the already formed char. This suggests that $FeCl_3$ does not promote reaction of nitriles during degradation of this resin. DDE also did not affect significantly the thermal stability of this material. In spite of the fact that DDE significantly increased the conversion of nitrile groups during polymerization, char yield and $T_{5\%}$ values are the same when compared with the samples polymerized in the absence of this curing agent [23]. Thermal properties of phthalonitrile-terminated polyimide and phthalonitrile resins cured in the presence of an aromatic diamine catalyst are shown in Table 2 for comparison. It is notable that phthalonitrile functional polybenzoxazines exhibit in all instances higher char yield in both, nitrogen and air, and highly comparable values of $T_{10\%}$. The polybenzoxazine based on bifunctional precursor **III** shows higher values of $T_{5\%}$ when compared with other high-performance phthalonitrile resins and also when compared with polybenzoxazines from monofunctional precursors **I** and **II**. The latter can be due to the lower extent of cross-linking upon polymerization of both the functionalities — single oxazine ring and the phthalonitrile group.

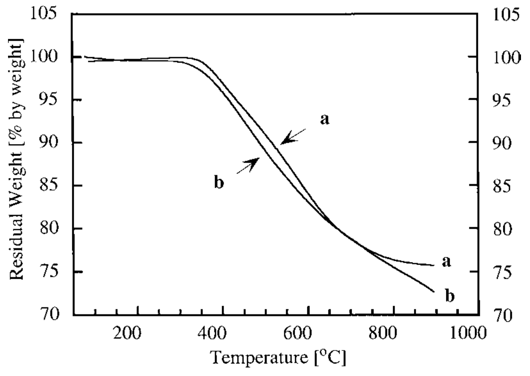


Fig. 4. TGA curves of polybenzoxazine **I**+5% DDE (a), **I**+5% $FeCl_3$ (b) in nitrogen.

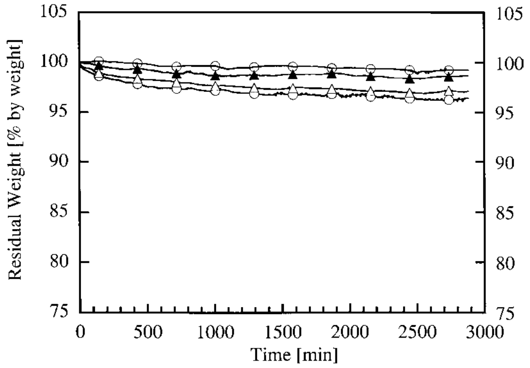


Fig. 5. Isothermal TGA curves of polybenzoxazine **I** in nitrogen for 48 h at 400°C (○), 360°C (△), 320°C (▲), 290°C (○).

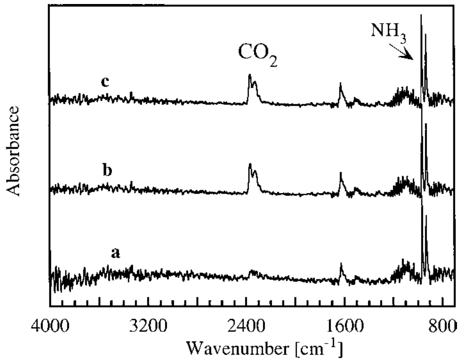


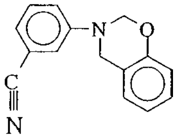
Fig. 6. FTIR spectra of the gas phase during degradation of polybenzoxazine **I** at 350 (a), 450 (b), 640°C (c).

Isothermal TGA experiment in Fig. 5 shows that polybenzoxazine **I** loses <5 wt.% of the initial weight at 400°C for an extended period of time — 48 h. This confirms high thermal resistance of this polymer. The char formation process involving phthalonitrile side groups was studied by means of TGA-FTIR interface analysis.

3.2. TGA-FTIR interface analysis

Only about 50% of all nitrile functionalities are consumed during the polymerization of phthalonitrile functional benzoxazines [23]. It is presumed that a process consuming all remaining nitrile functionalities takes place during the char formation when the rest of the cross-linked networks with Manmch bridge structure undergo thermal degradation. This assumption is confirmed by the FTIR spectra of the films heated at 250 and 600°C (not show here). The intensity of the band at 2225 cm^{-1} assigned to –C≡N decreased only by about 50% for a sample heated to 250°C. This band was completely consumed at 600°C with a new band appearing at 1750 cm^{-1}, which is assigned to C=O, suggests degradation of the Mannich bridge (not shown here) [23]. To further confirm the complete polymerization of phthalonitrile groups during the thermal degradation of related polybenzoxazines, evolved gases were analyzed by the TGA-FTIR interface and the respective spectra are shown in Fig. 6. The spectra were taken at different temperatures (different retention times) during the TGA run. The spectra show that only carbon dioxide represented by the doublet at 2328 and 2357 cm^{-1}, substituted benzene represented by bands at 1503, 1611 and 988 cm^{-1}, and ammonia assigned to the doublet at 923 and 950 cm^{-1} are released during the thermal decomposition of this material up to 800°C. Expectedly, the intensity of these bands increases with increasing degradation temperature. These degradation products are very likely the result of the Mannich bridge, –CH$_2$–NR–CH$_2$–, decomposition. Since there are no nitrile-containing compounds present in the evolved gases, it can be concluded that phthalonitrile functional groups were completely consumed during the char formation of this material. Also, there is no evidence of hydrogen cyanate present in the gaseous phase during the degradation of this material which makes them environmentally safe. Negligible concentration of substituted benzenes was observed in the gas phase during the degradation of this polymer. This is in contradiction to the results of the unfunctional aniline-based polybenzoxazines [25].

Fig. 7 shows for comparison FTIR spectra of the evolved gases from the degradation of the single nitrile functional polybenzoxazine derived from the monomer shown below.



This example was chosen to positively assign the peak position of the nitrile band in the gaseous phase and to eliminate the possibility that the remaining phthalonitrile functionalities of phthalonitrile-based

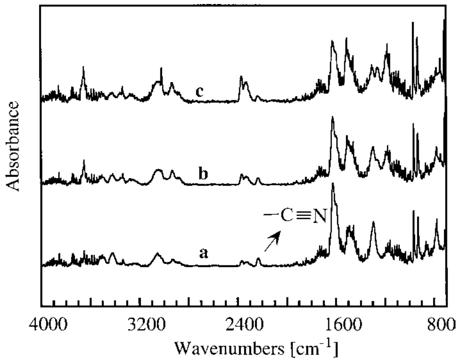


Fig. 7. FTIR spectra of the gas phase during degradation of metanitrile functional polybenzoxazine, 300 (a), 360 (b) and 450°C (c).

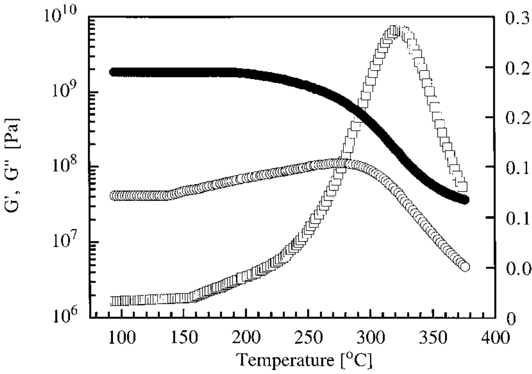


Fig. 8. DMA spectra of polybezoxazine **I**, *G*′ (●), *G*″ (○), tan *δ* (□).

polybenzoxazines could produce ammonia, carbon dioxide and benzene during degradation. In the initial stage of degradation (spectrum a), new bands at 3419, 1625 and 1294 cm^{-1} are observed in addition to the bands representing carbon dioxide, ammonia and benzene. These bands can represent primary or secondary amines [25]. Phenol or substituted phenols are found to be major degradation products at higher temperatures ranging from 360–450°C as represented by the bands at 3651, 1503 and 1181 cm^{-1} (spectra b and c) [25]. These bands were not found in the gas-phase spectra of phthalonitrile functional polybenzoxazine (Fig. 6). Apparently, metasubstituted nitrile does not react completely during char formation, since there is significant concentration of nitrile groups found in the gas phase as represented by the band at 2232 cm^{-1}. Therefore, this resin resulted in lower char yield and this will be discussed elsewhere [24]. There is no evidence of the band at 2232 cm^{-1} in the spectra of phthalonitrile-based polybenzoxazine in Fig. 6.

The cross-link network formation of this class of polybenzoxazines was further investigated by DMA.

3.3. Dynamic mechanical analysis (DMA)

Fig. 8 displays DMA spectra of polybenzoxazine based on monofunctional benzoxazine precursor **I**. The storage modulus (G') exhibits a value of 2.2 GPa at 100°C. Typical DMA spectrum of standard polybenzoxazines based on unfunctional primary amines–aniline exhibit sharp maximum of the dependence of loss modulus vs. temperature. DMA spectrum shown in Fig. 8 displays unusually broad dependence of loss modulus (G'') on temperature with the maximum around 278°C. Also, tan δ shows a broad peak with maximum around 319°C. Glass-transition temperature, T_g, can be determined from the maximum of G'' and for this sample T_g was higher than the curing temperature, T_{cure}, by 40°C.

Fig. 9 displays a DMA spectrum of polybenzoxazine **IV** based on a bifunctional benzoxazine precursor. The storage modulus shows a value of 1.9 GPa at 100°C and again loss modulus exhibits a broad maximum centered around 300°C and a broad maximum of tan δ around 330°C. The shift of the maxima of the loss modulus as well as tan δ to higher temperatures can also be explained by a higher degree of cross-linking of bifunctional precursor-based

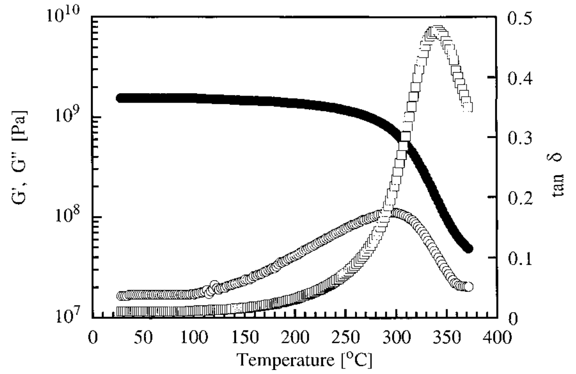


Fig. 9. DMA spectra of polybenzoxazine **IV**, *G*′ (●), *G*″ (○), tan *δ* (□).

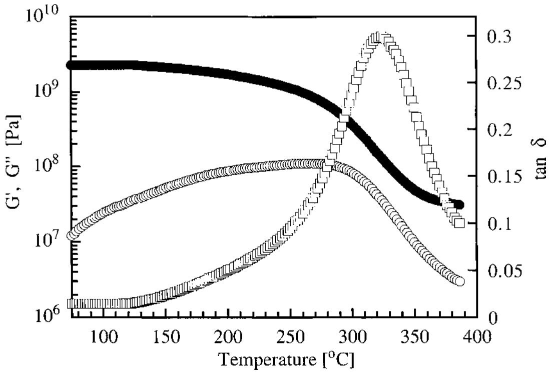


Fig. 10. DMA spectra of polybenzoxazine **I** cured in the presence of 5 wt.%DDE, G' (●), G'' (○), tan δ (□).

polymer. It can be concluded that, in this case also, T_g is higher than T_{cure} by 50°C.

DMA spectrum of the polybenzoxazine **I** polymerized in the presence of aromatic diamine (DDE) is shown in Fig. 10. No significant changes have been found, either in the position of the maximum or in the broadness of the dependence of loss modulus (G'') and tan δ on temperature. G'' shows a broad maximum around 275°C. The initial storage modulus has also a value of 2.3 GPa.

The values of the maxima of G'' and tan δ for all shown polymers are shifted to higher temperatures when compared with aniline-based polybenzoxazines [21]. The reaction of the phthalonitrile substituents in addition to the oxazine ring polymerization contributed to a higher degree of cross-linking and increase of T_g. The unusual broadness of the loss modulus and tan δ curves can then be explained by a very broad distribution of molecular weights or the nonuniform distribution of cross-links [26]. It has been reported that resins exhibiting a high and broad G'' transition have the ability to absorb energy associated with impact [27].

3.4. Flammability characterization

Flammability tests were performed on microscale samples using micro-cone calorimeter. The values of maximum peak heat release rate (PHR) and total heat release (THR) are compared with currently considered state-of-the-art low flammability polymer polyetherimide (PEI) and the other polymers as shown in Table 3. Phthalonitrile functional polybenzoxazines show one of the lowest values of the PHR and THR, which means they can be included into the class of low flammability materials.

Table 3
Flammability properties of phthalonitrile-functional polybenzoxazines and other polymers

Polymer	Peak μHRR (W/g)	Total μHRR (kJ/g)
Polybenzoxazine **I**	100.9	4.97
Polyetherimide Ultem™	187.4	6.72
Phenolic resin	80	6.5
PPS	400	11.2
Nylon	700	19.0

4. Conclusion

Highly thermally stable polybenzoxazines were prepared from phthalonitrile-terminated benzoxazine monomers. The reactive phthalonitrile terminal group contributed to the formation of highly thermally stable cross-linked structures as it was shown by dynamic and isothermal TGA. It was confirmed by TGA-FTIR study that the remaining nitrile groups, which did not react during polymerization, undergo further reaction during thermal degradation and form high char yields. Polymerization temperature of 250°C was sufficient to achieve material of high thermal stability and T_g in the range of 275 to 300°C. Additionally, these polymers also exhibit low flammability and can be included into a category of high-performance materials.

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References

[1] T.M. Keller, J. Polym. Sci. Part A: Polym. Chem. 26 (1988) 3199.

[2] T.T. Serafini, J. Appl. Polym. Sci. 16 (1972) 905.
[3] H.R. Lubowitz, US Patent, 3,528,950 (1970).
[4] T. Takekoshi, J.M. Terry, Polymer 35 (1994) 4874.
[5] S.B. Sastri, J.P. Armistead, T.M. Keller, Polymer 36 (1995) 1449.
[6] S.B. Sastri, T.M. Keller, K.M. Jones, J.P. Armistead, Macromolecules 26 (1993) 6171.
[7] W.E. Douglas, A.S. Overend, Eur. Polym. J. 27 (1991) 1279.
[8] W.T.K. Stevenson, I.I. Goldfarb, E.J. Soloski, M.J. Houtz, J. Appl. Polym. Sci. 42 (1991) 679.
[9] B.A. Reinhardt, F.B. Arnold, J. Polym. Sci., Chem. Ed. 19 (1981) 271.
[10] W.X. Huang, S.L. Wunder, J. Appl. Polym. Sci. 59 (1996) 511.
[11] V. Sankaran, S.C. Lin, C.S. Marvel, J. Polym. Sci., Chem. Ed. 18 (1980) 495.
[12] K. Mai, H. Zeng, .J. Appl. Polym. Sci. 53 (1994) 1653.
[13] T. Yoshida, Y. Abe, T. Masuda, T. Higashimura, J. Polym. Sci., Part A 34 (1996) 2229.
[14] D.J. Capo, J.E. Schoenberg, J. Sampe 23 (1987) 35.
[15] T.M. Keller, Polym. Comm. 28 (1987) 337.
[16] T.M. Keller, J. Polym. Sci., Chem. Ed. 26 (1988) 3199.
[17] T.M. Keller, T.R. Price, J. Macromol. Sci., Chem. A18 (6) (1982) 931.
[18] T.M. Keller, Polym. Mater. Sci. Eng. Prep. 58 (1988) 1039.
[19] S.B. Sastri, J.P. Armistead, T.M. Keller, Polym. Comp. 18 (1) (1997) 48.
[20] R.F. Boswell, A.C. Guy, F.B. Arnold, Proceedings NATAS, Cleveland, OH, 1998, p. 63.
[21] X. Ning, H. Ishida, J. Polym. Sci., Chem. Ed. 32 (1994) 1121.
[22] H.J. Kim, Z. Brunovska, H. Ishida, Polymer (in press).
[23] Z. Brunovska, H. Ishida (in preparation).
[24] Z. Brunovska, H. Ishida (in preparation).
[25] H.Y. Low, H. Ishida, Polymer (in press).
[26] K. Dusek, J. Smrckova, Proceedings PMSE, ACS Meeting, Dallas, TX, 1998.
[27] D.M. Crawford, J.A. Escarsega, Proceedings NATAS, Cleveland, OH (1998), p. 618.