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DEVELOPMENT AND CHARACTERIZATION OF NOVEL FIRE SAFE EPOXY RESINS

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Abstract: The curing system for newly developed solid state fire safe epoxy resins using dicyandiamide (DICY) was introduced. Composites of epoxy resins obtained from diglycidyl ether of 1,1-dichloro-2,2-bis(4-hydroxyphenyl)ethylene bisphenol-C (BPC) and bisphenol-A (BPA) epoxy resins in the reaction with BPC and BPA and DICY hardener were studied. Solid epoxy resins were synthesised by the use of two different heating methods: conventional and microwave reactor. The quantities of DICY additions were 0.5–5.0 %, optimum was found to be 3 %. Limited oxygen index (OI) tests for different epoxy resins and addition of flame – retardants were carried out. The highest value of OI was 34.6. As additional flame-retardants were used zinc stannates (ZS, ZHS). Evident OI increase was noted from 27.0 for classical epoxies, 34.6 for BPC cured epoxies and 44 for cured composites with the addition of Zn/Sn flame-retardants.

Keywords: fire-safety, oxygen index, flame retardants, epoxy resins, diglycidyl ethers, microwaves, dicyandiamide, zinc stannates.

1. Introduction

Recently construction industries like aviation and shipbuilding have been demanding more thermally stable and fire safe epoxy resins. In a real life it is difficult to prepare the material that would be totally incombustible, so the emphasis is usually on developing fire-safe materials and resins [1]. Extensive investigations on the application of chloral (trichloroacetic aldehyde) and its derivatives for polymer syntheses were carried out at the Warsaw University of Technology for the last 40 years [2, 3]. It

was proved that inexpensive chloral polymers were very effective as fire-safe materials. The most interesting of these is 1,1-dichloro-2,2-bis(4-hydroxyphenyl)ethylene (BPC). In 1962 the first Polish patent in this area was applied [4, 5]. There are also important developments in other directions [6, 7]. The Federal Aviation Administration (FAA) [1, 8] and University of Massachusetts Amherst [9] were carrying out intensive research in this field.

The FAA was evaluating the fire hazard of chlorobisphenol resins using modern fire performance test methods (*e.g.*, heat release rate in flaming combustion and pyrolysis combustion flow calorimetry) as part of an ongoing effort to identify cost-effective, zero heat release rate materials for next generation aircraft cabin interiors. Examples of these tests are presented in Fig. 1. The results were obtained in Federal Aviation Administration by heat release rate test measured according to ASTM – E906. The comparison between DGEBA and DGEBC were presented in spectacular way for different hardeners.

The study examined the fire, flammability, thermal, and mechanical properties of diglycidyl ethers of bisphenol A and diglycidyl ethers of bisphenol C (DGEBA and DGEBC) polymerized by four different mechanisms: (1) anionic ring opening polymerization using catalytic amounts of 2-ethyl-4-methylimidazole (EMI-24); (2) addition polymerization with aliphatic (triethylenetetramine-TETA) and aromatic (4,4'-metyhlenedianiline-MDA) amines; (3) catalyzed phenolic cure with the parent phenols (BPA and BPC); and (4) the dicyanate ester resin derived from bisphenol C (CEBPC). The last mentioned curing agent cyanite ester of bisphenol C was a very important invention carried out in the USA. The composites based on the above mentioned epoxy resins have been tested in

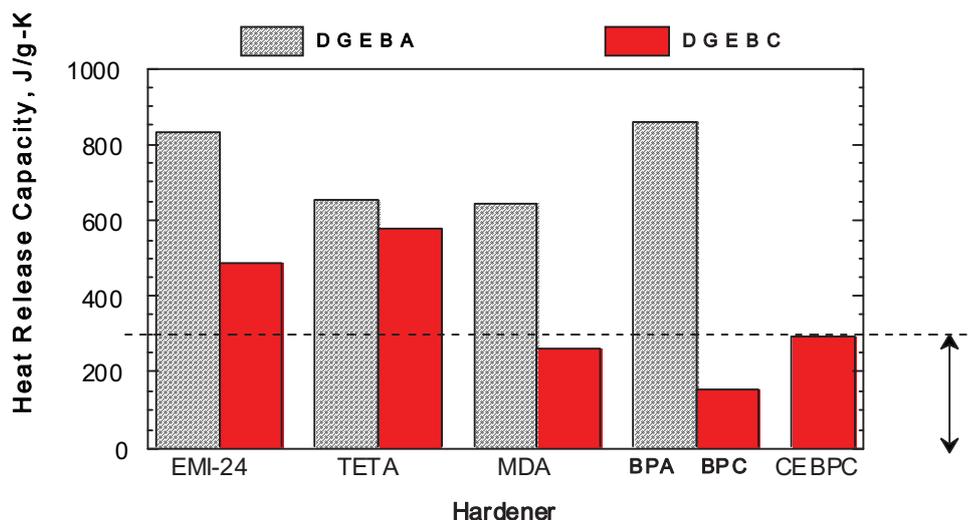


Fig. 1. Epoxy heat release capacities [1]

aviation as well as in ship construction. The investigations carried out with different curing agents allow reaching excellent mechanical and dielectrical properties of BPC epoxy resins and the highest values of fire retardancy. By way of comparison, none of the DGEBA systems passed the FAA heat release requirement of exhibited self-extinguishing characteristics in the UL 94 V test [8, 10].

Previous works [11, 12] have consisted in the synthesis of a few different epoxy resins based on low molecular weight commercial epoxy resins such as Epidian 5 (Sarzyna Poland) and diglycidylether of bisphenol-C (DGEBPC) resulting in high molecular-weight solid-state epoxies (the epoxy value stays low around 0.03–0.09; $M_w = 1700$ – 2300).

The most important development here presented is introduction of dicyandiamide (DICY) as a curing agent for fire-safe epoxy system [13].

2. Experimental

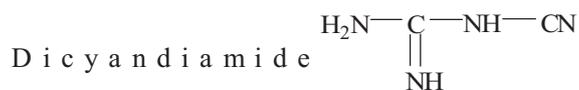
2.1. Materials

Two different bisphenols were used. Bisphenol A – 2, 2 bis(p hydroxyphenyl) propane (BPA) – commercially available from Blachownia Chemical Works (Poland) and bisphenol C – 1,1- dichloro-2,2-bis (4-hydroxyphenyl)ethylene (BPC) synthesized in our lab according to the description presented elsewhere [14].

Three different low molecular weight epoxy resins were used. Two commercial BPA epoxies ARALDITE – GY 250 from Huntsman Company Austria, Epidian 5[®] from Sarzyna Company (Poland), and one was prepared in our lab: DGEBPC (diglycidylether of bisphenol C). Diglycidyl ether of bisphenol C was prepared according to the description [2, 12].

ZS (zinc stannate) and ZHS (zinc hydroxystannate) were commercial products of Joseph Storey Co (UK).

Dicyandiamide (DICY) from Sigma Aldrich Company was used as a curing agent for the epoxy resins with a 3 % concentration.



was one of the first curing agents to be used with epoxy resins. It gives systems with pot lives of six months with liquid/solid resins by virtue of its insolubility in the resins at ambient temperatures and is considered to be a highly latent epoxy resin curing agent. When heated in the presence or absence of catalysts, rapid polymerization commences to yield high crosslinked molecules exhibiting high strength, moderate heat resistance, high solvent resistance, and excellent electrical insulating properties. High temperatures, however are required to initiate reaction, therefore DICY is normally used in conjunction with co-curing accelerators/catalysts as the uncatalyzed reaction with epoxy resins begins well above 423 K. The mechanism of curing epoxy resins with DICY is complex and involves initial reaction between all four active hydrogen of DICY with epoxy resin [13].

2.2. Procedure

Epoxy resins were synthesized through the fusion reaction, the base which consisted of a selection of low molecular weight epoxy resins were mixed up to homogeneous solution with, bisphenol A and bisphenol C – 1, 1-dichloro-2, 2-bis (4-hydroxyphenyl) ethylene 25 g of each of the epoxies: DGEBPA or DGEBPC were added with the mixture of bisphenols BPA/BPC according to

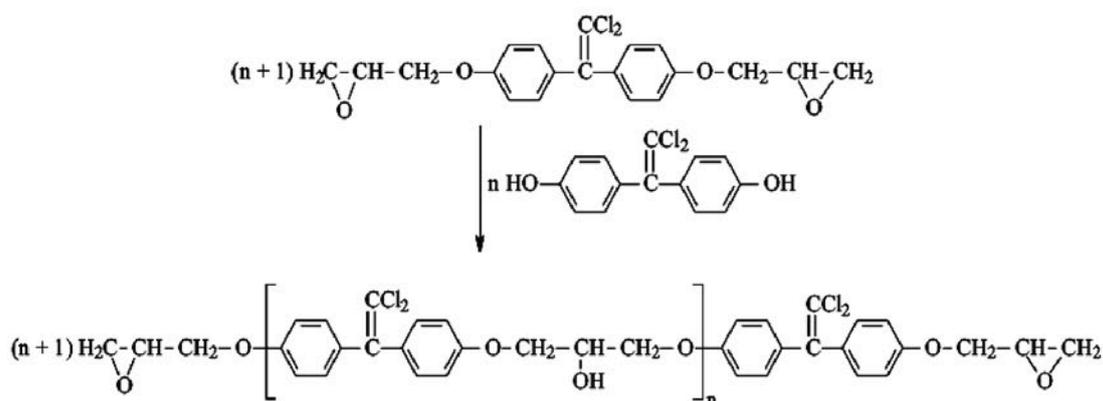


Fig. 2. Synthesis of fire safe epoxy resins

Table 1. The reactions (Fig. 2) between diglycidyl ethers and bisphenols A and C were carried out at 3 different temperatures 393, 418 and 443 K. The main reaction was carried out using Plazmatronika equipment (described below). In the next step epoxies and curing agents were warmed to temperatures 393, 418 and 443 K and mixed together by mechanical mixer with the rotations 2000 rpm in different quantities according to Table 1.

The evidence of these solid state epoxies by FTIR and NMR were published in the previous papers [11, 12].

Two different heating systems were used: conventional electrical and novel microwave reactor [15-17]. Several epoxies were heated using the same microwave reactor – Multi-mode Microwave Reactor “Plazmatronika” (microwave frequency is 2.45 GHz, maximum of microwave power is 600 W), with connected thermometer. The power of the reactor during synthesis was programmed on constancy level 40 % independent from the mixture. Reactions were conducted in an atmosphere of argon.

Several syntheses were carried out using different epoxies and bisphenols, temperature and varied component concentrations (concentration of BPC from 0 to 100 % is given in Table 1).

Table 1

Comparison of conventional method in the entire range of the epoxy composition for 418 K

No.	Weight ratio of bisphenols A/C	Epoxy number, mol/100g
1	0/100	0.119
2	25/75	0.118
3	40/60	0.116
4	50/50	0.112
5	60/40	0.110
6	75/25	0.109
7	100/0	0.109

2.3. Methods

Investigations were carried out using Polish standards. Limiting oxygen index (OI) was measured after PN-76/C-89020. Epoxy numbers were determined after PN-74/C-89085 and melting points after PN-87/C-89085/04.

Oxygen index (OI) is the flammability test based on the technique of clamping a certain volumetric concentration of specimen in a tube, and introducing a mixture of oxygen and nitrogen, the relative concentrations of which can be gradually varied at measured rates. A flame is applied to the top of the sample until it ignites, and then is withdrawn. If the flame extinguishes, the concentration of oxygen is increased and the sample is re-ignited until it finally continues to burn. The concentration of oxygen at this point is the index of

flammability, calculated as $OI = \frac{O_2}{O_2 + N_2}$, where O_2 is

the minimum volumetric concentration of oxygen which will just support combustion, and N_2 is the associated nitrogen concentration. Test was carried out due to PN-76/C-89020 (ASTM D 2863-74).

Epoxy number. This is the most common analytical measurement that is carried out on uncured epoxy resin. Methods for the assay of epoxy content involve the halogen-acid cleavage of the epoxy ring to yield a halohydrin. The reaction is quantitative. The sample of epoxy resin was dissolved in the mixture of organic and halogen acid. The excess of halogen acid was titrated by sodium hydroxide solution.

Softening point according to standard is based on the ball and ring method. In this method the sample is held in a horizontal ring with a steel ball on the top of it. The temperature is raised at a prescribed rate and the softening point is that temperature when the ball has moved downwards by a distance of 2.5 cm under its own weight.

3. Results and Discussion

3.1. Conventional Fusion Method

The reaction mixture consisted of low-molecular weight epoxy resin and mixture of bisphenol C and bisphenol A which were mixed to the form of homogeneous solution. Fig. 3 presents the comparison between the reactions carried out at 393, 418 and 443 K. The medium curve represents composition No 2 from Table 1. Other curves represent analogous composition cured at 393 and 443 K.

The fusion procedure was tested at 3 different temperatures 393, 418 and 443 K. The reaction at 393 K was too slow and at 443 K the colour of the tested samples was too dark. The medium temperature 418 K was chosen as an optimum one. The reaction proceeded with satisfactory speed and final colour was acceptable. In the function of raising temperature the colour of the epoxy composition is darkening going from straw- yellow to dark brown. It is caused by hydrogen chloride release and transparency is decreasing. Our objective was to get not too dark colour with some transparency. Very similar colour evaluation is generally applied in the case of PVC products.

3.2. Microwave Method

According to the procedure described in the experimental part of this paper a few syntheses of solid epoxy resins were carried out. The recipes of these syntheses are presented in Table 2.

Detailed description is presented in Table 3.

Table 2

The weight ratio of mixture bisphenol A/bisphenol C for 25 g low molecular weight epoxy resin (reaction temperature 443 K)

No.	Bisphenol A, wt %	Bisphenol C, wt %	Ratio bisphenol A/bisphenol C, g/g
1	100	0	8.889/0
2	75	25	6.667/2.394
3	50	50	4.445/4.788
4	25	75	2.222/7.182
5	0	100	0/9.575

The synthesis of fire safe solid epoxy resin (microwave method) of weight ratio bisphenol A/bisphenol C = 25/75.

Composition:

Epoxy resin25 g

Bisphenol A.....2.710 g

Bisphenol C.....9.766 g

Method of synthesis: Application of microwaves

Temperature of synthesis: Controlled 442–444 K

Power of microwave reactor: 40 %

The comparison of the results obtained by using microwave and conventional methods is presented in Fig.4.

The use of microwave radiation as novel heating medium alternative to the conventional methods proved to provide a quicker and more effective synthesis [11]. The microwave method is especially profitable for chemical compounds which are sensitive to long-lasting high temperatures exposure.

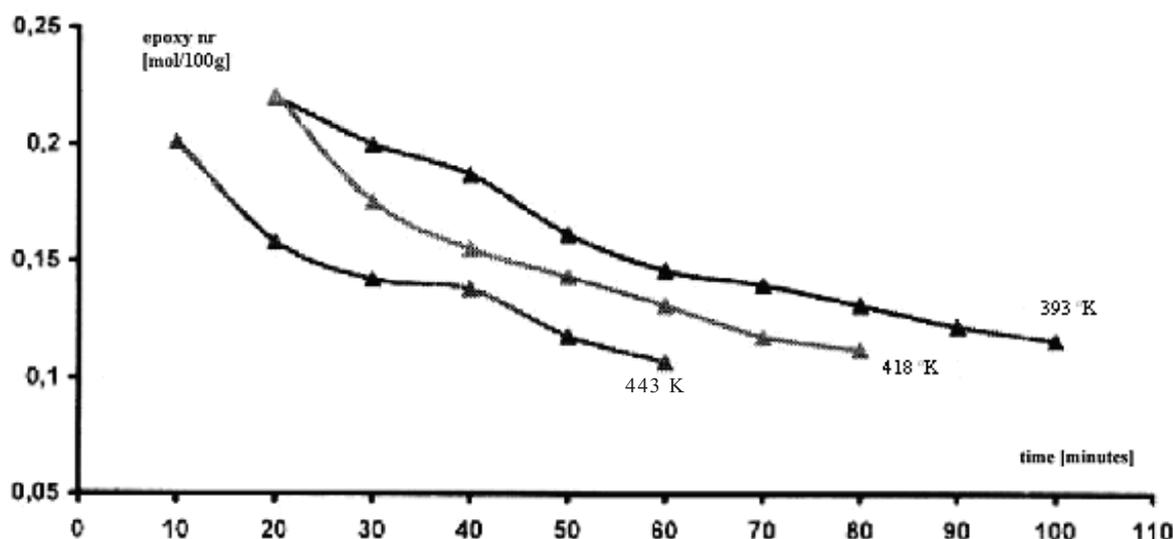


Fig. 3. Comparison of reactions at 393, 418 and 443 K in plot of epoxy number (Y-axis) vs. reaction time (X-axis)

Table 3

Conditions of epoxy resin syntheses

No.	Sample temperature, K	Temperature of microwave oven, K	Reaction time, min	Resin weight, g	Epoxy number, mol/100g	<i>M</i>	Melting temperature, K
1	467	443	10	0,621	0.156	1282	-
2	463	442	20	0,600	0.116	1724	-
3	458	444	30	0,599	0.089	2247	-
4	439	278	179	0,459	0.086	2326	-
5		443	50	0,622	0.077	2597	342–344

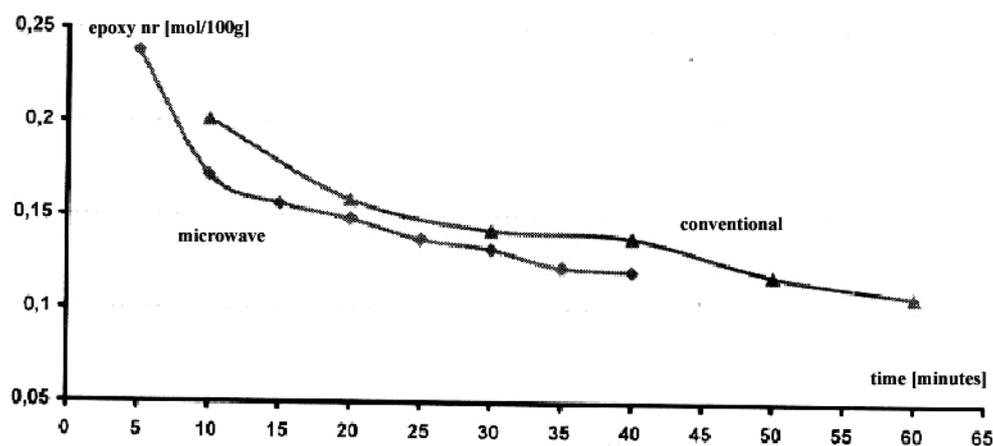


Fig. 4. Comparison of epoxy numbers by microwave and conventional method

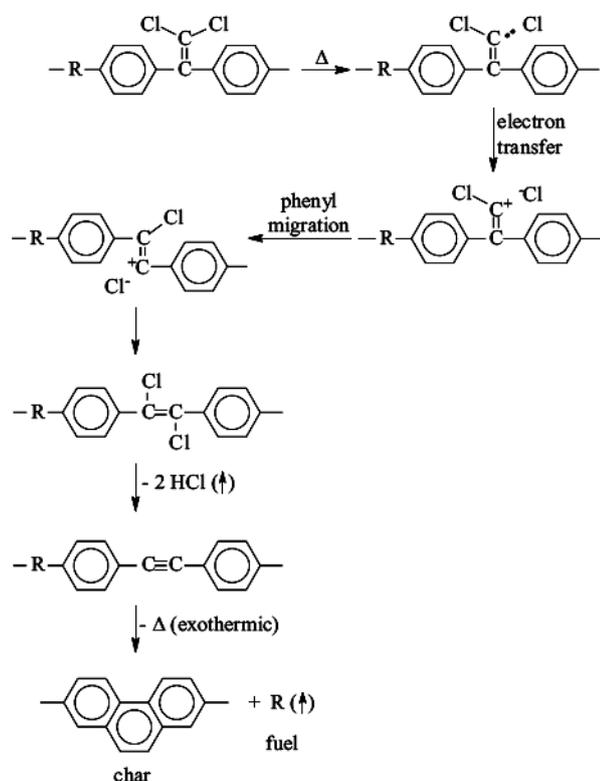


Fig. 5. Thermal degradation mechanism of chloral-based condensation polymers

Fig. 5 represents decomposition of chloral derivatives during fire. Thermal degradation is thought to proceed via dichlorostilbene intermediate to yield two moles of hydrochloric acid and diphenylacetylene in the polymer backbone. Diphenylacetylene undergoes a strong exothermic reaction, liberating fuel gases *R* and forming a solid polyaromatic char in nearly quantitative yield. These processes explain very good fire-safety properties received for solid epoxy resins.

The best parameters of obtained results for cured fire safe epoxies were as follows: (after heating in microwave oven during 50 min at 443 K) [11]. Epoxy number is 0.077 mol/100g; molecular weight *M* is 2590; melting point 342–344 K.

3.3. Studies on Cured Samples

12 g of obtained fire-safe solid state resins were chosen as an example for this publication. The bisphenols ratio BPA/BPC was 40/60 mas % and temperature of reaction was 418 K. The quantity of curing agent was variable from 0.5 to 5 % of used resin. The results are presented in Table 4.

The best results for OI were obtained for the added quantity 3 % of curing agent DICY.

The changes in OI presented in Table 4 can be explained, as follows:

Table 4

**Curing time due to the quantity
of dicyanodiamide curing agent at 403 K**

No. of sample	Quantity of curing agent, %	Curing time, min	Oxygen indexes, OI unit
1	0.5	uncured	-
2	1.0	25	30.3
3	1.5	22	31.5
4	2.0	18	32.0
5	2.5	15	34.1
6	3.0	15	34.6
7	3.5	15	34.2
8	4.0	16	34.0
9	4.5	18	34.1
10	5.0	20	34.0

Table 5

Oxygen indexes due to the quantity of bisphenol C at 403 K

No. of sample	Quantity of bisphenol C, %	Curing time, min	Oxygen indexes, OI unit
2.1	0	15	27.0
2.2	25	15	28.3
2.3	40	15	30.3
2.4	50	15	32.2
2.5	75	15	34.4
2.6	100	15	35.8

Table 6

The effect of ZS/ZHS on OI of fire-safe epoxy samples

OI							
ZS, wt %				ZHS, wt %			
0	1	2	3	0	1	2	3
34.6	35.8	42.15	44.02	34.6	35.4	42.07	43.85

1. In the first step by increasing of DICY from 0.5 to 3 % the OI of samples were going raising from 30.3 up to 34.6 due to crosslinking of resin (flammability is getting down).

2. Further increasing of DICY causes that OI is getting down due to incorporating of DICY excess, which is more flammable than halogen containing epoxy resin.

The next step of investigation was testing the influence of BPC on OI. The results are presented in Table 5.

These results are predictable. Increasing of BPC content is increasing of chlorine amount in epoxy resin and chlorine which is causing fire retardancy [2, 3]. Epoxy resins combustibility has been reduced by application of BPC in the synthesis.

OI of epoxy resin derived from BPC was measured and found to be significantly better than derived from bisphenol A for each of the systems compared in the study. The epoxy resins are less flammable when they contain less bisphenol A segments in the polymer structure.

The obtained OI were 27 for BPA epoxy resins cured by DICY were growing up and reached 35.8 for 100 % of added BPC.

3.4. The Effect of ZS and ZHS Addition

The preliminary results of OI of cured by 3 % of DICY fire-safe epoxy samples after the addition of ZS and ZHS are presented in Table 6. As low molecular weight

epoxy resin diglycidyl ether of BPC (DGBPC) and mixture of BPA/BPC in the ratio 25/75 was used.

The literature study gave complete information about unsaturated polyester resin composites with zinc stannates (ZS-ZnSnO₃ and ZHS-ZnSn(OH)₆) [18, 19]. According to pyrolytic tests it could be predicted, that Sn caused transfer of halogen (bromine or chlorine) to gaseous phase as SnX_n (where X is Br or Cl). This compound reacts with the creation of volatile SbX₂ and gaseous HX (HBr or HCl). In the case of bromine there is evident difference in boiling points for SnBr₄ – 475 K and SnBr₂ – 893 K. Thus, in the gaseous phase we have bromine in the form of SnBr₄. HBr and HCl may be more effective as radical scavengers created in the fire. This fact explains more effective action of ZS or ZHS than SnO₂.

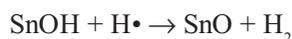
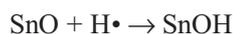
The mechanism can be presented as follows:

1. Polymer +R-CH₂-Br, where R is hydrocarbon chain;

2. R-CH₂-Br + [ZnSn(OH)₆] → ZnSnO₃ + H₂O !
Zn₂SnO₆ + SnBr_x + hydrocarbons, where x = 2 or 4;

3. SnBr₂ + H₂O → (SnO, SnO₂) + HBr.

Also radicals H•, OH•, and RO• formed during polymer destruction can react with SnO and SnO₂.



The above described reactions created so-called catalytic action [20-22].

4. Conclusions

The cured by dicyandiamide DICY samples of fire-safe epoxies on the base of diglycidyl ethers and BPA/BPC mixtures have good fire-resistance increasing OI up to about 36. The method of obtaining solid-state resins may be carried out by conventional and microwave way. Microwave method is more effective and quicker and will be recommended in case of industrial implementation of the project here presented. Preliminary test pointed out the advantage of the use of zinc stannates ZS or ZHS. The addition of 2-3 % of these compounds enhanced OI of resins from 35 to 44 and also very effectively reduced smokes during fire.

We decided to use these ZS and ZHS compounds as FR for our chlorine contains epoxy resin based on the above cited positions from literature [18-22]. We decided also to use ZS and ZHS as FR according to literature data in the 1-3 wt % amounts only. According to pyrolytic tests it was predictable that Sn caused transfer of halogen (bromine or chlorine) to gaseous phase as SnX_n (where X

is Br or Cl). This compound reacts with the creation of volatile SbX₂ and gaseous HX (HBr or HCl). In the case of bromine there is an evident difference in boiling points for SnBr₄ 475 K and SnBr₂ – 893 K. Thus, in the gaseous phase we have bromine in the form of SnBr₄. HBr and HCl may be more effective as radical scavengers created in the fire. This fact explains more effective action of ZS or ZHS than SnO₂ [23].

References

- [1] Lyon R.: Ultra fire-resistant thermoset polymers. Fire Research Program, Federal Aviation Administration, Technical Center Atlantic City International Airport, NJ 08405, 2005.
- [2] Brzozowski Z.: *Polimery*, 1986, **31**, 99.
- [3] Brzozowski Z.: Assistant professor theses, Warsaw University of Technology, 1986.
- [4] Brzozowski Z. and Porejko S.: Polish pat. 47 344, Publ. Dec. 15, 1964.
- [5] Brzozowski Z. and Porejko S.: Pat. UK 1 051 335, Publ. July 26, 1963.
- [6] Factor A. and Orlando C.: *J. Polym. Sci. Chem.*, 1980, **18**, 579.
- [7] Rusanov A.: *Progress in Polym. Sci.*, 1994, **19**, 589.
- [8] Lyon R., Castelli L. and Walters R.: Proc. BCC Conf., Stamford, Ct, USA, May 21-23, 2001, 102.
- [9] Zhang P. Westmoreland R., Farris R. *et al.*: *Polymer*, 2002, **43**, 5463.
- [10] Lyon R.: *Fire Resistance Mat.: Research Overview*, 2000, DOT/FAA/AR/00/42.
- [11] Brzozowski Z., Staszczak S., Rupinski S. *et al.*: *J. Appl. Polym. Sci.*, 2006, **100**, 3850.
- [12] Brzozowski Z., Staszczak S., Hadam L. *et al.*: *Polimery*, 2007, **52**, 29.
- [13] Ellis B. (ed): *Chemistry and technology of epoxy resins*: Chapman&Hall, London 1994.
- [14] Brzozowski Z., Kielkiewicz J., Rawski T. *et al.*: Polish pat. 86401, Publ. Nov. 15, 1976.
- [15] Bogdal D.: ScD-habilitation, Krakow University of Technology, Krakow 1999.
- [16] Forsyth A. and Whittaker K.: *J. Appl. Polym. Sci.*, 1999, **74**, 2917.
- [17] Fu B. and Hawley M.: *Polym. Eng. Sci.*, 2000, **40**, 2133.
- [18] Cusack P., Monk A., Pearce J. and Reynolds S.: *Fire and Materials*, 2005, **14**, 23.
- [19] Cusack P., Heer M. and Monk A.: *Polym. Degrad. Stab.*, 1997, **58**, 229.
- [20] Grassie N., Johnston A. and Scotney A.: *Eur. Polym. J.*, 1981, **17**, 589.
- [21] Shen K. and Sprague R.: *Plastics Compounding*, 1982, **5**, 67.
- [22] Kicko-Walczak E.: DSc. thesis, Warsaw University of Technology, 2003.
- [23] Costa L., Luda M. and Trossarelli L.: *Polym. Degrad. Stab.*, 2000, **68**, 67.

РОЗРОБКА І ХАРАКТЕРИСТИКА НОВІТНІХ ПОЖЕЖНО-БЕЗПЕЧНИХ ЕПОКСИДНИХ СМОЛ

Анотація. Розглянуто затверджену систему нових пожежно-безпечних твердих епоксидних смол синтезованих з використанням дициандіаміду (ДЦДА). Композити епоксидних смол одержані з дигліциділового етеру 1,1-дихлор-2,2 біс(4-гідроксифеніл)етилену бісфенолу С (БФС) і епоксидних смол бісфенолу А (БФА) за реакцією між БФС і БФА з використанням як затвердника ДЦДА. Тверді епоксидні смоли синтезовані з використанням двох різних методів нагріву: звичайного і у мікрохвильовому реакторі. Кількість ДЦДА коливалась від 0,5

до 5,0 %. Визначено оптимальну концентрацію затвердника, яка становила 3 %. Визначено кисневий індекс (КІ) для різних епоксидних смол. Найвищий КІ становив 34,6. Як додаткові сповільнювачі полум'я використовували станати цинку. Показано зростання КІ з 27,0 для класичних епоксидів до 34,6 для затверджених епоксидів і до 44 для затверджених композитів з додатком Zn/Sn сповільнювачів.

Ключові слова: пожежно-безпечний, кисневий індекс, сповільнювачі полум'я, дигліциділовий етер, мікрохвилі, дициандіамід, станати цинку.