ZBIGNIEW K. BRZOZOWSKI[1)3)*)], SYLWIA STASZCZAK[2)], ŁUKASZ HADAM[2)], WOJCIECH ZATORSKI[3)], SŁAWOMIR RUPIŃSKI[1)], DARIUSZ BOGDAŁ[4)]

Fireproof, solid state epoxy resins

Summary — Solid state epoxy resins were synthesized in the reactions of the systems: 1,1-dichloro-2,2-bis(4-hydroxyphenyl)ethylene (BPC II) and 2,2-bis(4-hydroxyphenyl)propane (bisphenol A), mixed in various weight ratios, with one of two low-molecular weight epoxy resins, Epidian 5® or diglycidylether of 1,1-dichloro-2,2-bis(4-hydroxyphenyl)ethylene (DGEBC II). Additionally the series of the samples synthesized with use of DGEBC II but with addition of red phosphorus as flame retardant were prepared. It was found, on the basis of limiting oxygen index (*LOI*) measurements, that the flammability of the samples decrease (higher values of *LOI*) with increase in BPC II weight part in the mixture with bisphenol A, for all the series of samples prepared. Solid state resins synthesized with the use of DGEBC II were less flammable than similar samples with bisphenol A. Addition of red phosphorus increased significantly *LOI* values, however, caused deterioration of optical properties of the resins investigated. The samples characterized with low flammability were selected for the syntheses with addition of zinc stannate (ZS) or zinc hydroxystannate (ZHS) as flame retardants. The values of *LOI* of the products obtained were determined (Table 2). It was found that the addition of 2—3 wt. % of ZS or ZHS significantly improves *LOI* values not causing the deterioration of optical properties.
Key words: solid state epoxy resins, 1,1-dichloro-2,2-bis(4-hydroxyphenyl)ethylene, flame retardants, oxygen index.

OGNIOODPORNE, STAŁE ŻYWICE EPOKSYDOWE
Streszczenie — W reakcjach układu 1,1-dichloro-2,2-bis(4-hydroksyfenylo)etylenu (BPC II) i 2,2-bis(4- -hydroksyfenylo)propanu (bisfenol A) zmieszanych w różnych stosunkach masowych i jednej z dwu małocząsteczkowych żywic epoksydowych: "Epidian 5®" lub eter diglicydowy 1,1-dichloro-2,2-bis(4- -hydroksyfenylo)etylenu (DGEBC II) zsyntetyzowano stałe żywice epoksydowe [równanie (1), tabela 1]. Dodatkowo przygotowano serię próbek zsyntetyzowanych z użyciem DGEBC II ale z dodatkiem fosforu czerwonego jako antypirenu. Na podstawie pomiarów indeksu tlenowego (*LOI*) stwierdzono, że palność próbek spada (wyższe wartości *LOI*) wraz ze wzrostem udziału masowego BPC II w mieszaninie z bisfenolem A w każdej otrzymanej serii próbek (rys. 1). Stałe żywice zsyntetyzowane z udziałem DGEBC II były mniej palne niż analogiczne próbki z udziałem bisfenolu A. Dodatek fosforu czerwonego znacznie zwiększał wartości *LOI* natomiast powodował pogorszenie właściwości optycznych badanych żywic. Wybrane próbki charakteryzujące się małą palnością wybrano za podstawę do syntez z użyciem cynianu cynku (ZS) lub hydroksycynianu cynku (ZHS) jako antypirenów i wyznaczono wartości *LOI* otrzymanych produktów (tabela 2). Ustalono, że dodatek 2—3 % mas. ZS lub ZHS zdecydowanie podwyższa wartości *LOI* nie powodując pogorszenia właściwości optycznych.
Słowa kluczowe: stałe żywice epoksydowe, 1,1-dichloro-2,2-bis(4-hydroksyfenylo)etylen, antypireny, indeks tlenowy.

Recently, the requirements of the manufacturing and construction industries concerning the thermally stable and fire safe epoxy resins have grown dramatically. In a real life it is difficult to prepare the material that would be totally incombustible, so some research works focus on self-extinguishing epoxy resins [1, 2]. These resins initially burn when exposed to a naked flame, however when the flame is removed the resins stop burning so they are effectively self-extinguishing. To improve these properties, additional materials are added: these materials are called flame retardants. Typical flame retardant material include in its structure such atoms as: chlorine, bromine, phosphorus, nitrogen, boron, antimony, molybdenum or silicon [3].

Extensive investigations on the application of chloral and its derivatives for polymer syntheses were carried out at the Warsaw University of Technology for the last 40 years [4—11]. It was proved that not expensive chloral

[1)] Warsaw University of Technology, Faculty of Chemistry, Koszykowa 75, 00-662 Warsaw.
[2)] Napier University, School of Engineering, Merchiston Campus, 10 Colinton Rd, Edinburgh, EH10 5DT.
[3)] Central Institute for Labour Protection — National Research Institute, Czerniakowska 16, 00-701 Warsaw.
[4)] Cracow University of Technology, Warszawska 24, 31-155 Cracow.
[*)] E-mail: Zbigbi@ch.pw.edu.pl

polymers were very effective as fire-safe materials. The most interesting of these is 1,1-dichloro-2,2-bis(4-hydroxyphenyl)ethylene (BPC II). In 1962 the first Polish patent in this area was applied [5]. There are also important developments in others places [12, 13]. Now the polymers obtained from chloral derivatives — polish original invention — are in the center of interest in scientific and industrial circles. Among them the Federal Aviation Administration (FAA) [1, 14, 15] and University of Massachusetts Amherst [13] are carrying out intensive research in this field. The composites based on the above mentioned epoxy resins have been used in aviation as well as in ship construction *e.g.* submarine vessels. The investigations carried out with different curing agents let reach [16] the excellent mechanical and dielectrical properties and the highest values of fire retardancy. The new polymers in comparison with those obtained from 2,2-bis(4-hydroxyphenyl)propane (bisphenol A) are characterized by better thermal and chemical resistance, increase in glass transition temperature and the evident decrease in flammability.

In the investigations of the fire resistant parameters of plastics the key areas are: limiting oxygen index (*LOI*), flame start temperature, temperature classification as well as the temperature of inflammation.

Our previous work has consisted of the syntheses of a few different epoxy resins based on low molecular weight commercial epoxy resins like Epidian 5 (Sarzyna, Poland) and diglycidylether of BPC-II (DGEBC II) resulting in high-molecular weight solid state epoxy resins (the epoxy value stays low around 0.03—0.09 and molecular weight 1700—2300) [17]. The other works were done before in Poland [18] and in the USA [19].

In Technical University of Cracow [20] and in the Industrial Chemistry Research Institute [21] the investigations on the improvement of epoxy resins' fire-retardancy were carried out. Fire retardant epoxy compositions modified with halogen free retardants were developed. As fire retardants mainly phosphorus-nitrogen compounds such as ammonium polyphosphates or melamine polyphosphates, allowing to utilize the synergy of phosphorus-nitrogen actions, were used. The favorable use of halogen containing polymers were confirmed during last BCC conference in Stamford [22].

In order to increase the fire retardancy of BPC epoxy resins we decided to test the influence of such fire retardants as red phosphorus or zinc stannates expecting also synergistic effects.

EXPERIMENTAL

Materials

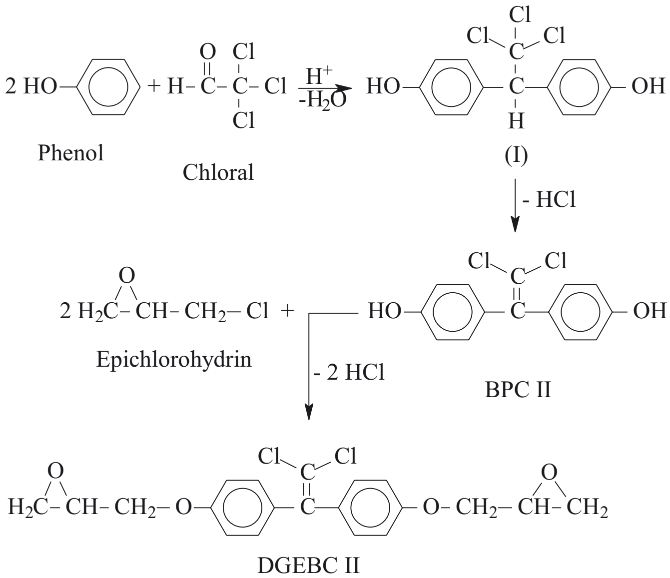
2,2-Bis(*p*-hydroxyphenyl)propane (bisphenol A) was commercially available from Blachownia Chemical Works (Poland).

1,1-Dichloro-2,2-bis(4-hydroxyphenyl)ethylene (BPC II) was synthesized in our laboratory according to the description [23, 24].

Two different low molecular epoxy resins were used:

— Epidian 5® — basic epoxy resin from Sarzyna Company (Poland) (epoxy number 0.48—0.51 mol/100 g, viscosity at 25 °C maximally 30.000 mPa · s),

— diglycidylether of BPC II (DGEBC II) in crystalline form was prepared in our laboratory according to the Scheme A [17, 25].



Scheme A. Synthesis of DGEBC II

Red phosphorus (trade name Exolit RP 652) from Clariant Co. in form of brown-red paste was thixotropic blend of castor oil with stabilized, micro encapsulated red phosphorus.

Zinc stannate (ZS) and zinc hydroxystannate (ZHS) — commercial products of Storey Co. (UK).

Syntheses of solid state epoxy resins

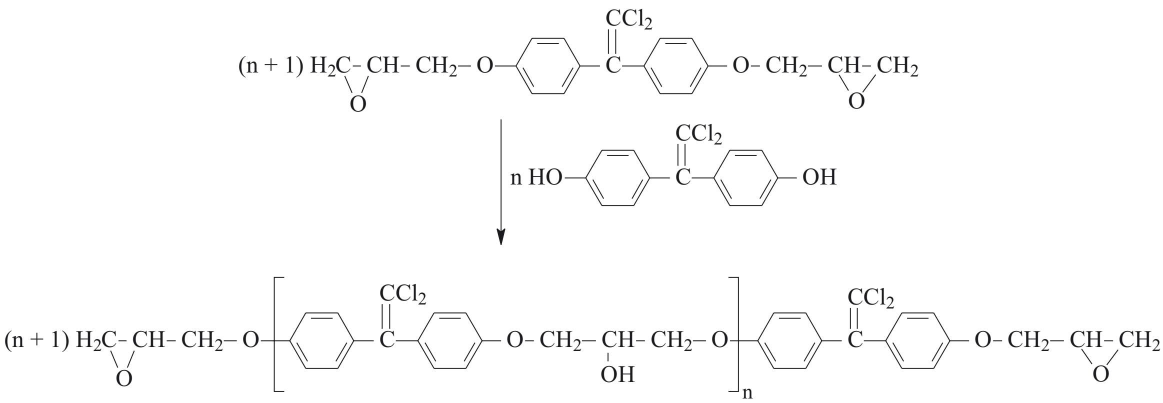
Solid state epoxy resins were synthesized through the fusion reaction. The reaction mixture consisted of low-molecular weight epoxy resin and mixture of BPC II and bisphenol A which were mixed to the form of a homogeneous solution. Three series of samples were prepared differing in the type of low-molecular epoxy resin or addition of red phosphorus. In every series the BPC II/bisphenol A weight ratio in mixture of total mass 10.5 g were changed. The compositions of samples are specified in Table 1.

The exemplary course of reaction is described by equation (1).

Preliminary tests were carried out and afterwards the mixtures consisted of BPC II/bisphenol A 75/25 and 100/0 with DGEBC II were chosen to be tested with ZS

T a b l e 1. Compositions of prepared solid state epoxy resins

Series	Low-molecular weight epoxy resin		Amount of red phosphorus, g	BPC II/bisphenol A weight ratio						
	type	amount, g								
1	Epidian 5®	25	0							
2	DGEBC II	25	0	0/100	25/75	40/60	50/50	60/40	75/25	100/0
3	DGEBC II	25	4							



(1)

and ZHS flame retardants. 25 g of DGEBC II was homogenized with 10.5 g mentioned mixtures and finally one of two flame retardants, ZS or ZHS in quantity 0, 1, 2 or 3 wt. % per total mixture of epoxy resin was added.

The fusion procedure was tested in 3 different temperatures 120, 145 and 170 °C. The reaction in 120 °C was too slow and in 170 °C the color of tested samples was too dark. The medium temperature 145 °C was chosen as optimum one. The reaction run with satisfactory speed and final color was not too dark.

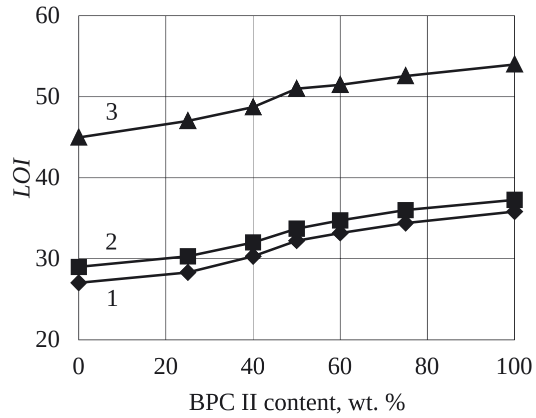


Fig. 1. The effect of BPC II concentration in binary mixtures BPC II/bisphenol A on limiting oxygen index (LOI) of solid state epoxy resin for series 1, 2 and 3 (see Table 1)

Method of testing

Investigations of limiting oxygen index (*LOI*) were obtained using Polish standard PN-76/C-89020.

RESULTS AND DISCUSSION

The Figure 1 displays the changes of the *LOI* dependent on the concentration of BPC II in binary mixture BPC II-bisphenol A. The concentration of BPC II which can be consider as a flame retardant have a significant influence on *LOI* value. The growth of BPC II concentration cause a decrease in epoxy resin flammability for all used epoxy systems. The lowest *LOI* was observed when Epidian 5 was used to a synthesis (series 1). The better results were obtained for series 2 with using of DGEBC II. The sample with a *LOI* value of around 37.3 was achieved in the process of DGEBC II with pure BPC II.

The differences between DGEBC II and Epidian 5 are precisely presented in Fig. 1. The evident synergistic effect is seen.

Red phosphorus used in series 3 was selected as very efficient flame retardant for epoxy resins. The use of that fire-retardant heavily increased *LOI* and improved the quality of the sample surface but negatively affected the optical properties (color, transparency) because the epoxy resin acquired the color of the flame retardant (dark brown). The flame retardant based on red phosphorus added to epoxy resin decreased the viscosity of the composition (because of the liquid support of castor oil) and easily formed a homogeneous mixture with solid-state epoxy resin.

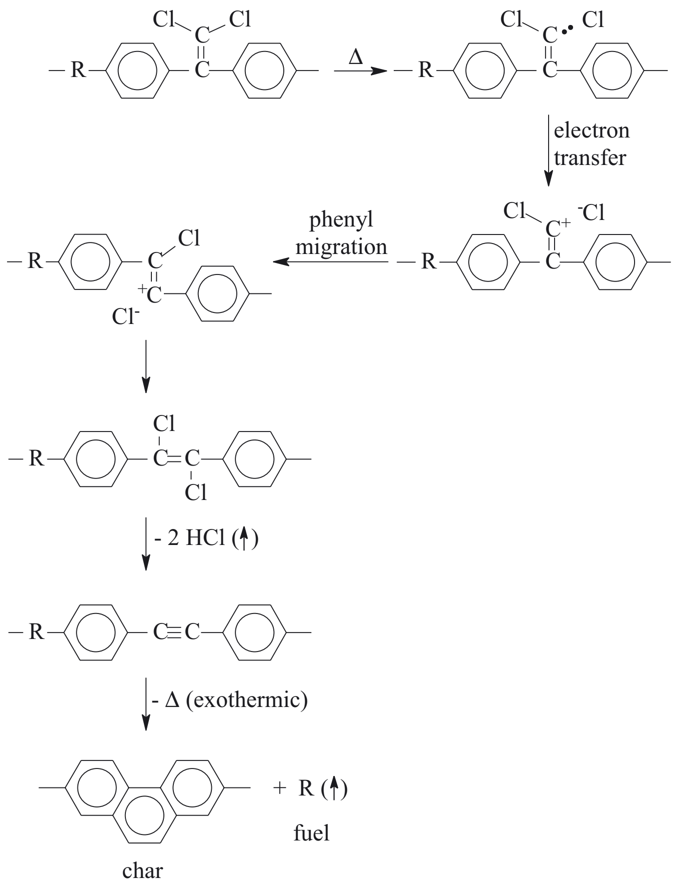
To study the effects of other flame retardants *i.e.* ZS or ZHS on *LOI* value the samples based on DGEBC II and 75/25 or 100/0 of BPC II/bisphenol A were chosen. Those samples even without the additives showed relatively high *LOI* values: 36 and 37.3, respectively.

As it can be seen from Table 2 the addition of ZS or ZHS give a very good effect on *LOI* increase. These fire retardants are very effective just in amounts 2—3 wt. %. Such small total concentration of flame retardant has slight effect on the optical properties.

T a b l e 2. Effect of flame retardant (ZS or ZHS) addition on limiting oxygen index (*LOI*) of solid state epoxy resins synthesized using DGEBC II

BPC II/bisphenol A weight ratio	LOI							
	ZS, wt. %				ZHS, wt. %			
	0	1	2	3	0	1	2	3
75/25	36.00	37.54	43.13	45.53	36.00	38.35	41.20	42.97
100/0	37.30	38.75	44.00	46.40	37.30	39.00	42.16	43.52

For the sample with addition of ZHS, the results displayed an almost linear relationship between concentration of flame retardant and *LOI*. The highest *LOI* was measured for the samples containing BPC II without bisphenol A and 3 wt. % of ZS. The flame retardant substance slightly affects the viscosity of the composition and due to the small concentration it is easy to reach a homogeneous mixture with epoxy resins. The results clearly show that ZS and ZHS let give beneficial fire retardancy to epoxy resins similarly as it is described in the literature for polyester resins [26].



Scheme B. Thermal degradation mechanism of chloral-based condensation polymers

The exceptional fire retardancy of BPC II epoxy resin is illustrated in the Scheme B [19, 27]. 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 properties received for solid epoxy resins.

CONCLUSIONS

— Epoxy resins' combustibility has been reduced by application of BPC II in the synthesis. The fire behavior of epoxy resin derived from BPC II was measured and found to be significantly better than derived from bisphenol A for each of systems compared in the study. The epoxy resins are less flammable when contain in the polymer structure less bisphenol A segments.

— *LOI* of solid state epoxy resins synthesized with using of Epidian 5 or DGEBC II were compared. The use of DGEBC II give the products less flammable than conventional epoxy resins.

— DGEBC II epoxy resins synthesized with addition of red phosphorus showed better *LOI* values than those with use of ZS or ZHS as flame retardants, but used red phosphorus quantity was close to 10 wt. % while amounts of ZS or ZHS were only up to 3 wt. %.

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