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Phenol-formaldehyde resols modified by boric acid

RAPID COMMUNICATION

Summary — Phenol-formaldehyde resol resins with improved thermal stability and flame retardancy were prepared by introducing boric acid into the matrix of PF precondensates at the condensation stage. The modified PF resols had small amounts of free monomers and high solid mass content. The thermogravimetry of cured, modified PF resols showed enhanced thermal stability in comparison with unmodified ones indicating the role of boric acid in improving thermo-oxidative resistance. Besides, the determined limited oxygen index values indicated the significantly decreased flammability of the modified resins.

Key words: phenol-formaldehyde resol, boric acid, thermal stability, flame retardancy, limited oxygen index.

REZOLOWE ŻYWICE FENOLOWO-FORMALDEHYDOWE MODYFIKOWANE KWASEM BOROWYM

Streszczenie — Zsyntetyzowano rezolowe żywice fenolowo-formaldehydowe (PF) o zwiększonej odporności termicznej i zmniejszonej podatności na palenie poprzez wbudowanie w strukturę żywicy na etapie kondensacji kwasu borowego (rys. 1, tabela 4). Modyfikowane rezole PF charakteryzują się małą zawartością wolnych monomerów i dużą zawartością części nielotnych (tabela 1). Na podstawie badań derywatograficznych ustalono, że utwardzone, modyfikowane żywice PF wykazują zwiększoną stabilność termiczną w stosunku do żywicy niemodyfikowanej (tabela 2). Jak potwierdzono na podstawie widm IR i analizy GPC (tabela 3) jest to wynikiem wbudowania się cząsteczek kwasu borowego w strukturę żywicy co zwiększa odporność żywicy na procesy termooksydacyjne.

Słowa kluczowe: rezole fenolowo-formaldehydowe, kwas borowy, odporność termiczna, ognioodporność.

The phenol-formaldehyde (PF) resol resins formed from phenol and formaldehyde in the presence of alkali have a wide range of applications, depending on the final molecular weight, viscosity and structure. Low molecular weight phenolic resol resins are used to impregnate the paper for laminates to reduce their water absorption. High molecular weight resins are used for plywood glues, thermal insulations and moldings [1—3].

The rapid growth of PF resins applications is the reason of extensive research with the aim to improve their thermal and flame retardancy properties. PF resins with improved thermal stability and flame retardation were prepared by introducing flame retardant elements such as phosphorus and bromine at the monomer stage, followed by condensation with formaldehyde [4—5].

A boron-modified phenolic resin flowable at useful processing temperatures was prepared in the solvent-less reaction of triphenyl borate and paraformaldehyde [6].

The new PF resins containing itaconic acids, itaconimides and their homopolymers, showing a good thermal stability, are reported in the paper [7].

The propargyl ether was also used as a modifier of PF resin, improving its thermostability. Synthesis and properties of so modified resins are described in the work [8].

The aim of this work was to use boric acid for synthesis of PF resols and to determine their selected physicochemical properties and thermal stability of modified resins. The idea of using boric acid for modification of phenolic resins is not new. Gao J. et. al. studied the possibility of use of so modified resins as matrices for laminates [9].

EXPERIMENTAL

Materials

The following materials were used in this work:

— Phenol (a.p., POCh, Poland)

— Formaldehyde (as 37 % aqueous solution, POCh, Poland)

— Boric acid (a.p., POCh, Poland)

— Sodium hydroxide (a.p., POCh, Poland)

Preparation of phenol-formaldehyde resin modified by boric acid

Synthesis of the modified resol was performed at a formaldehyde/phenol molar ratio (F/Ph) of 1.2. Sodium hydroxide (0.014 mol) was used as a catalyst. A mixture of phenol (1 mol) and formaldehyde (1.2 mol) as aqueous solution (37 wt. %) were placed into 250 cm^3 three-neck round-bottomed flask equipped with mechanical stirrer, thermometer and reflux condenser. The flask content was stirred for 1 h at 70±1 °C. After that, the mixture was dehydrated inside the same flask under vacuum (1.33 kPa) at 75±1 °C for 45 min. In the next step the boric acid (0.3 mol) as a modifier was added and temperature was raised to 110±1 °C. The mixture was heated for 40 min. The dehydration of modified resol was performed under vacuum (1.33 kPa) at 90±2 °C until a total extraction of water. The given procedure was repeated for other amounts of boric acid (0.5 and 0.8 mol) used as modifier (see Table 1).

Curing

The investigated resins were cured at 170 °C in the oven for 1 h.

Analytical methods

^1H NMR spectra of modified resins were recorded using TESLA Spectrometer AN 80 MHz, former Czechoslovakia (in d_6 — DMSO) with TMS internal standard.

FT-IR spectroscopy was used for characterization of modified resins. FT-IR spectra were recorded using PARAGON 1000 Perkin Elmer spectrometer, using the potassium bromide pellet method.

The thermal properties of cured resins were determined using Paulik-Paulik system MOM derivatograph (Hungary) in air, in the temperature range 20—1000 °C, using 0.2 g sample and recording time 100 min. The amplification of 1/15 for differential thermal analysis (DTA) and 1/10 for differential thermal gravimetry (DTG) was applied.

A gel permeation chromatograph (GPC-KNAUER) with a differential refractometer detector was used in order to analyse the modified PF resols. A Plgel Mixed-E three columns (300 × 7.5 mm) at 30 °C were employed. Analytical grade, dried THF was used as a solvent.

The concentration of injected samples was 1 mg/mL and flow rate was 0.8 mL/min.

The contents of free monomers (phenol and formaldehyde) were measured according to the standards: PN-75/C-89044 and PN-92/C-89424 respectively, solid mass content according to PN-ISO 8618:1999 and curing time — in agreement with ISO 8987 standard.

The flammability of cured samples were measured according to PN-82/C-89023 standard.

Limited oxygen index (*LOI*) was determined following the PN-76/C-89020 procedure.

RESULTS AND DISCUSSION

The use of boric acid as a modifier of resol PF resins resulted in the resins with advantageous properties (Table 1). Their solid mass content varied in the range 90—95 wt. %, content of free formaldehyde was about ten times lower in comparison with unmodified resin. The content of free phenol was also decreased (3—4 times) in relation to unmodified resin.

Table 1. Physicochemical properties of phenol-formaldehyde resols modified by boric acid

Properties of the resin	Amount of modifiers, mol			
	0	0.3	0.5	0.8
Solid mass content, wt. %	61.20	95.98	92.63	89.85
Free formaldehyde content, wt. %	2.60	0.21	0.19	0.14
Free phenol content, %	6.25	1.50	1.71	2.13
Curing temperature, °C	160	172	130	130

The high solid mass content indicates a small content of water and low molecular weight compounds. Commonly, the presence of them unfavorably influences the curing process causing bubbling and cracks on the surface.

In turn, the content of free formaldehyde and phenol essentially influences the processing and useful properties of the resins. The presence of phenol reduces the resin resistance to light, meanwhile the free formaldehyde is harmful for health during processing and the use of products.

It was proved by means of FT-IR and ^1H NMR spectroscopy that boric acid builds into the structure of resin firstly by means of hydroxymethyl groups of prepolymer PF; secondly by hydroxyl groups of phenol. This result can be illustrated by FT-IR analysis. The characteristic absorption peak of benzyl hydroxy group $-CH_2-OH$ at 1017 cm^{-1}, very large for unmodified resin, became very small for the modified one. In the FT-IR spectra of modified resins absorption peaks at 1384—1386 cm^{-1} from vibrations of boron-oxygen bond also appear.

The results of gel permeation chromatography also confirm the fact of building of the modifier into the resol structure. It is clear from the growth of number-average molecular weight ($\overline{M}_n$) and weight-average molecular weight ($\overline{M}_w$) values of the modified resins in comparison with unmodified ones (Table 2).

T a b l e 2. Results of GPC analysis of phenol-formaldehyde resins modified by boric acid

Amount of modifier, mol	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
0	340	1165	3.37
0.3	568	1265	2.23
0.5	521	1098	2.11
0.8	604	1437	2.38

T a b l e 3. Thermal properties of unmodified and modified PF resins after curing

Amount of modifier, mol	T_p *) °C	$T_{5\,\%}$ **) °C	$T_{20\,\%}$ **) °C	$T_{50\,\%}$ **) °C	T_{max} ***) °C
0	140	140	470	750	985
0.3	120	160	530	980	980
0.5	140	230	540	990	990
0.8	160	140	520	990	980

*) T_p — temperature of beginning decomposition of the sample.
**) $T_{x\,\%}$ — temperature at which x wt. % of the sample evaporated.
***) T_{max} — temperature of maximum decomposition rate.

Thermal stability of the cured unmodified and modified resins (Table 3) shows the rise of this stability after building of the modifier into the structure of macromolecule.

The rise in modifier amount gives the increase in the temperature of decomposition beginning as well as the growth of temperature of weight loss: $T_{5\,\%}$, $T_{20\,\%}$, $T_{50\,\%}$ except the resin modified with 0.8 mol of boric acid. The temperature of maximum decomposition rate (T_{max}) generally remains unchanged.

T a b l e 4. Limiting oxygen index (*LOI*) of the modified PF resols

Amount of modifier, mol	0	0.3	0.5	0.8
LOI, %	29.12	47.39	57.02	59.15

The results of investigation of flammability of cured resins (Fig. 1) show that the length of burnt section of sample decreases with growth of amount of introduced boric acid. This indicates that the modifier acts as an inhibitor in the process of resin burning. Limited oxygen index (*LOI*) may be considered as a measure of samples flammability. Results in Table 4 show that the rise of modifier content gives the increase in *LOI* that corresponds to the decrease in flammability of the resins. It agrees well also with the results of samples burning that were illustrated in Fig. 1.

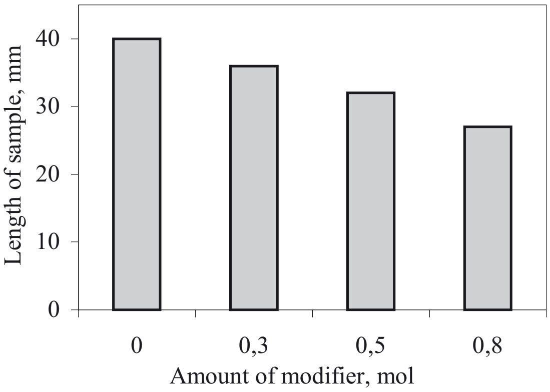

Fig. 1. Dependence of length of burned part of sample on the amount of modifier

CONCLUSION

The use of boric acid as a modifier of PF resin causes the decrease in free monomers content and the rise in solid mass content in comparison with the unmodified one.

The increase in incorporated modifier amount results in the growth of thermal resistance of modified resins, simultaneously their flammability becomes smaller.

The advantage of the boric acid as a modifier is the nontoxicity of the resulting resin compositions as well as of their burning products, contrary to the other well-known flame retardants like bromine.

REFERENCES

1. Knopp A., Pilato L. A.: "Phenolic resins: chemistry, application and performance — future directions", New York, Springer, 2000.
2. Reghundhan N. C. P.: *Progr. Polym. Sci.* 2004, **29**, 401.
3. Żmihorska-Gotfryd A.: *Polimery* 2004, **49**, 408.
4. Rosy A., Pillai C. K: *J. Appl. Polym. Sci.* 1994, **54**,429.
5. *Pat. USA* 3 352 744 (1967).
6. Abdalla Mohamed O., Ludwick A., Mitchell T.: *Polymer* 2003, **44**, 7353.
7. Pyriadi T. M., Berzinji A. Z.: *Desig. Monom. Polym.* 2003, **6**, 115.
8. Reghundhan Nair C. P., Bindu R. L., Ninan K. N.: *J. Macromol. Sci. Part A* 2003, **40**, 357.
9. Gao J., Liu Y., Yang L.: *Polym. Deg. Stab.* 1999, **63**, 19.

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