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Epoxy-carbazole compositions

Part I. COMPOSITIONS WITH 9-(2,3-EPOXYPROPYL)CARBAZOLE

RAPID COMMUNICATION

Summary — Compositions of low-molecular weight epoxy resin Ruetapox 0162 mixed with various amounts of 9-(2,3-epoxypropyl)carbazole (EPK) have been prepared and cured by isophorone diamine. Mechanical, thermal and photoluminescence properties of obtained materials were determined. It was found that low-molecular weight epoxy resin is an excellent dispersing matrix for carbazole groups, which secures suitable mechanical properties, low combustibility and high thermal stability of prepared materials. Moreover, it was observed that the addition of 10 wt. % of EPK improves compression strength by 15%, flexural strength by 33% and also slightly decreases water absorption. Thin film forming ability and optic properties, characteristic for isolated carbazole molecules (photoluminescence maxima at 352 and 368 nm), point at the possibility to use studied materials for light-emitting diodes (LED) construction.
Key words: epoxy resins, 9-(2,3-epoxypropyl)carbazole, light-emitting diodes, mechanical properties, thermal properties, photoluminescence properties.

In connection with the immense development of electronics and optoelectronics there has been a general increase in demand for new, modern materials showing photo- and electroconductive properties. Since the beginning of nineties of 20th century, organic materials, especially polymers, have attracted much attention because of their potential application in the construction of electrophotographic devices, LCD displays, automotive lighting, *etc.* It is well known that carbazole, its derivatives and polymers based on these molecules have good photo- and electroactive properties [1—5]. The preparation of polymers with carbazole units is also widely described in a number of publications and patents [6—12]. However, carbazole-based materials, obtained in polymerization, copolymerization or blending processes, show rather low stability during oxidation at not too high thermal decomposition temperature, in addition its mechanical properties are also insufficient. Thus, our purpose was to disperse glycidyl carbazole derivatives in the epoxy resin matrix and use such compositions as the hole-transporting and light-emitting layer in multilayer light-emitting diodes (LED) [13—15]. Epoxy-carbazole compositions are homogeneous due to the co-curing reactions of glycidyl derivatives, epoxy resin, and amine hardener. They show strong absorption in the ultraviolet spectral region and high photoluminescence efficiency, characteristic for carbazole, as well as excellent mechanical properties (*e.g.* compression, tensile and flexural strength), high thermal stability and good film-forming ability typical for epoxy coating systems.

EXPERIMENTAL

Materials

— Ruetapox 0162 (commercial grade) — practically pure hydroxyl group free diglycidyl ether of bisphenol A (average epoxy value 0.570 eq/100 g, hydrolysable chlorine content <0.2%), from Bakelite AG;

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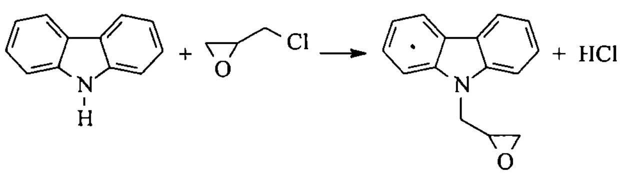
— Aradur 46 (commercial grade) — formulated isophorone diamine adduct (H^+ active equivalent 95 g/eq) from Vantico AG;

— Carbazole, epichlorohydrin and methyltrioctylammonium chloride (pure grade) from Fluka.

Epichlorohydrin was distilled before use, other materials were used without any additional purification.

Synthesis of 9-(2,3-epoxypropyl)carbazole

9-(2,3-epoxypropyl)carbazole (EPK) was synthesized in the reaction of carbazole and epichlorohydrin as described in [1] [equation (1) in interphase system acetone



(1)

+ KOH/K_2CO_3, catalyst — $NCH_3(C_8H_{18})_3^+Cl^-$, temp. 50—55°C, 3h] and purified by crystallization from ethanol.

Preparation of epoxy-carbazole compositions

EPK was dried to a constant mass, powdered in a ceramic mortar and sieved through the sieves (0.25 mm mesh size). Mixed compositions made of Ruetapox 0162 with various amounts of EPK (5, 10 and 15 wt. %) have been prepared. Homogeneity of solid EPK dispersions in the liquid resin was reached by mixing of the compositions for 20 min using mechanical stirrer and next holding them for 12 hours at temperature of 40°C. Epoxy-carbazole compositions prepared are highly viscous liquids ready to co-cure and stable enough to store for a long time without sedimentation of EPK.

Curing conditions

Mixed compositions of Ruetapox 0162 and EPK were cured by isophorone diamine (in amount adequate to average epoxy value determined every time for each cured composition) for 24 hours at room temperature and post-cured for 24 hours at 80°C.

Methods

— Mechanical properties of obtained compositions, *e.g.* flexural (ISO 178), compressive (ISO 604) and tensile strength (ASTM D 638) were determined by means of Zwick 1445 testing machine.

— Hardness was established with Zwick equipment model 3106 by the ball indentation method (ISO 2039-1).

— Water absorption was evaluated according to ISO 62.

— The curing processes were studied using Netzsch DSC 200 calorimeter calibrated with an indium reference. Samples of mixed compositions were scanned from 30 to 250°C with heating rate of 10 deg/min, in argon atmosphere.

— Glass transition temperatures of cured materials were established also using DSC method.

— Thermal stability (ISO 7111) of crosslinked compositions were determined using Netzsch TG 209 thermogravimetric analyser at a heating rate of 10 deg/min, in argon atmosphere (temperature range: 30—600°C).

— Flammability (characterized by oxygen index) was determined using standard test equipment according to the procedure described in ASTM D 2863.

— Photoluminescence spectra were recorded using Shimadzu RF-5000 fluorescence spectrophotometer (excitation wavelength = 264 nm); samples were prepared in the form of thin films employing spin-coating method.

RESULTS AND DISCUSSION

The idea of this research was to use low-molecular weight epoxy resin as a matrix for dispersion of carbazole molecules. Epoxy resin was chosen because of:

— commonly known outstanding mechanical properties and thermal stability,

— self-levelling ability that should make it easy to form thin films,

— we did not expect any photoluminescence activity of unmodified resin.

Additionally, EPK was applied because of its glycidyl group, which makes co-crosslinking reaction with resin and amine hardener possible. In spite of the fact that EPK is a solid compound, mixing it in amount up to 15 wt. % with the liquid resin gives homogeneous and stable compositions.

Liquid epoxy-carbazole compositions are also completely miscible with isophorone diamine and no phase separation or sedimentation process has been observed. Using DSC method we studied the crosslinking process and it was found that addition of EPK does not affect temperature of the peak maximum, ranged from 102 to 106°C. There are notable differences in the value of heat of curing (ΔH_c) depending on the EPK contents (Table 1).

These studies are in agreement with results of the average epoxy equivalent weight determination, *i.e.* 0.570 for pure epoxy resin and 0.546, 0.536, 0.534 for compositions containing 5, 10, 15 wt. % of the carbazole additive, respectively. EPK as a monofunctional compound reduces the functionality of epoxy resin, the consequence of that is a decrease in exothermic heat effect of the crosslinking reaction.

We supposed that the chosen small amount of carbazole additive added to the epoxy resin would be enough to set photoluminescence ability to this resin and should not decrease the mechanical strength of studied compo-

T a b l e 1. The effect of EPK concentration on the properties of epoxy-carbazole compositions co-crosslinked in the reaction with isophorone diamine

Properties	Concentration of EPK, wt. %			
	0	5	10	15
Tensile strength, MPa	61.85	57.47	62.05	51.46
Compression strength, MPa	72.00	64.30	82.10	78.60
Flexural strength, MPa	52.90	64.05	70.50	64.60
Hardness, N/mm^2	98.04	110.29	100.84	106.95
Oxygen Index, %	21.26	21.13	21.13	21.06
Heat of curing ΔH_c, J/g	302	309	233	235
Water absorption after 20 days, %	0.8029	0.8566	0.7705	0.7772

sition. As compared with properties of unmodified Ruetapox 0162, we observed that addition of EPK in amount of 10 wt. % improves the compression and flexural strength of epoxy-carbazole compositions respectively by 14% and 33% (Table 1). At the same time, modification of the epoxy resin with EPK does not improve the tensile strength; the lowest value was noted for the sample with 15 wt. % of EPK. In general, the composition containing 10 wt. % of EPK shows the best mechanical features, except for hardness. About 12% increasing of hardness was found for Ruetapox 0162 with 5 wt. % of the carbazole additive. A clear fall of glass transition temperature (*Tg*) has been found for all cured epoxy-carbazole materials (Fig. 1).

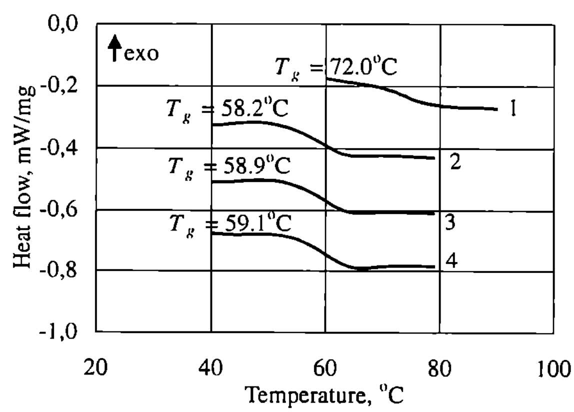


Fig. 1. The effect of EPK concentration on T_g value of crosslinked epoxy-carbazole compositions. Concentration of EPK: 1 — 0 wt. %, 2 — 5 wt. %, 3 — 10 wt. %, 4 — 15 wt. %

We have observed a decrease in T_g by ~13°C from 72°C for epoxy resin to 58.2—59.1°C for mixed compositions.

There is no difference in the flammability between unmodified resin and studied compositions. Oxygen Index value is kept at a constant level of about 21% (Table 1). On the other hand, mixed epoxy-carbazole materials are characterised by lower thermal stability than the crosslinked Ruetapox 0162 (Table 2).

T a b l e 2. The effect of EPK concentration on the thermal stability and char residue of epoxy-carbazole compositions cured with isophorone diamine*)

Concentration of EPK, %	*IDT*, °C	$T_{10\%}$, °C	$T_{20\%}$, °C	$T_{50\%}$, °C	Char residue %
0	177	285	361	383	13.7
5	162	259	363	385	13.9
10	166	265	358	383	15.7
15	161	255	356	381	11.8

*) Explanations of symbols — see text.

A decrease in initial decomposition temperature (*IDT*) is to 10°C for the composition containing 10 wt. % of EPK and to about 16°C for other materials. It was however observed, that differences in 20% and 50% decomposition temperature ($T_{20\%}$ and $T_{50\%}$, respectively) between studied compositions are very small and in the second case even insignificant. It could be stated that although the thermal decomposition of modified epoxy resins starts earlier, it does not proceed faster or more rapidly.

We have also checked the water absorption — important property of coating materials, from the practical point of view. The water absorption of the studied materials and the pure epoxy resin is low and comparable and does not depend significantly on EPK content (Table 1).

Strong absorption in the ultraviolet spectral region and high photoluminescence efficiency, characteristic for carbazole and its derivatives, were observed for mixed materials (Fig. 2).

It results, from the photoluminescence spectrum, that:

— as we predicted the crosslinked Ruetapox 0162 does not show photo-activity; trace luminescence comes

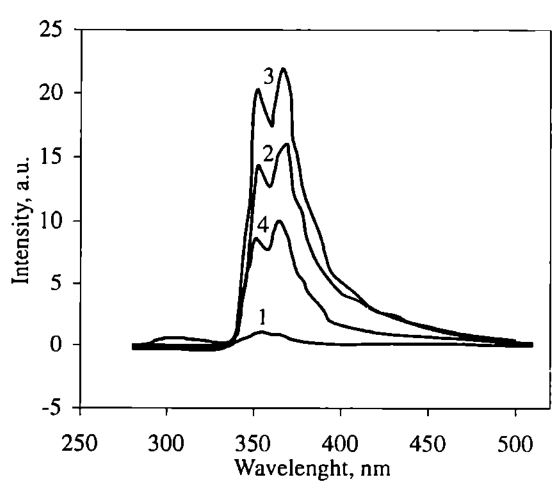


Fig. 2. The effect of EPK concentration on photoluminescence spectrum of crosslinked epoxy-carbazole compositions (excitation wavelength λ = 264 nm). Concentration of EPK: 1 — 0 wt. %, 2 — 5 wt. %, 3 — 10 wt. %, 4 — 15 wt. %

rather from the impurities (remains of the synthesis of bisphenol A),

— there are two maxima of photo-luminescence below 400 nm, at 352 nm and at 368 nm, characteristic for isolated carbazole molecules in solution,

— also in this case, the composition with EPK concentration of 10 wt. % reveals optimal properties. The photoluminescence spectrum, characteristic for carbazole solutions, proves that the epoxy resin used is a sufficient matrix, which eliminates mutual interactions of carbazole molecules and excimers formation [15, 16].

CONCLUSIONS

In a simple process we obtained homogeneous polymers with the carbazole molecules chemically bonded to the low-molecular weight epoxy resin. Results of our investigation show that low-molecular weight epoxy resin is an excellent dispersing matrix for EPK, which secures suitable mechanical properties, low combustibility and high thermal stability of new materials. Moreover, it was observed that the addition of 10 wt. % of EPK let obtain the composition showing the best set of properties between all systems investigated. This phenomenon undoubtedly need an explanation. Excellent thin film forming ability and high photoluminescence efficiency, characteristic for isolated carbazole molecules (two maxima placed below 400 nm), point at the possibility to use studied materials for the LED construction, comparable with other photoactive layers.

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REFERENCES

1. Akhmedov Kh. M., Karomiv Kh. S., Shcherbakova I. M., Porshev Yu. M., Cherkashin M. I.: *Usp. Khim.* 1990, **59**, 738, (English translation in: *Russ. Chem. Rev.* 1990, **59(5)**, 425).
2. Romero D. B., Schaer M., Leclerc M., Adès D., Siove A., Zuppiroli L. Z.: *Synth. Met.* 1996, **80**, 271.
3. Tamulaitis G., Gulbinas V., Undzenas A., Valkunas L.: *J. Lumin.* 1999, **82**, 327.
4. Sun R. G., Wang Y. Z., Wang D. K., Zheng Q. B., Epstein A. J.: *Synth. Met.* 2000, **111—112**, 403.
5. Kim D. Y., Cho H. N., Kim C. Y.: *Prog. Polym. Sci.* 2000, **25**, 1089.
6. Stéphan O., Vial J.-C.: *Synth. Met.* 1999, **106**, 115.
7. Shim H.-K., Kim H.-J., Ahn T., Kang I.-N., Zyung T.: *Synth. Met.* 1997, **91**, 289.
8. Bogdał D., Warzała M., Pielichowski J., Sanetra J.: *Polimery* 1999, **44**, 146.
9. Zheng H., Zhang R., Wu F., Tian W., Shen J.: *Synth. Met.* 1999, **100**, 291.
10. Jin S.-H., Kim W.-H., Song I.-S., Kwon S.-K., Lee K.-S., Han E.-M.: *Thin Solid Films* 2000, **363**, 255.
11. Abe S. Y., Bernede J. C., Delvalle M. A., Tregouet Y., Ragot F., Diaz F. R., Lefrant S.: *Synth. Met.* 2002, **126**, 1.
12. Bogdał D., Yashchuk V., Pielichowski J., Stępień I., Ogul'chansky T., Warzała M., Kudrya V.: *Polimery* 2002, **47**, 279.
13. Czub P., Mazela W., Pielichowski J.: *Materials (S-5/P-70)* of The Polish Chemical Society XLIII Annual Conference, Łódź 10—15.09.2000.
14. Mazela W., Czub P., Pielichowski J.: *Prace Naukowe Instytutu Technologii Organicznej i Tworzyw Sztucznych Politechniki Wrocławskiej* 2001, **50(23)**, 446.
15. Mazela W., Pielichowski J., Czub P., Sanetra J.: *Prace Naukowe Instytutu Technologii Organicznej i Tworzyw Sztucznych Politechniki Wrocławskiej* 2001, **50(23)**, 400.
16. Sanetra J.: Fizyczne właściwości układów polimerowych zawierających grupę karbazolową w aspekcie zastosowania ich w diodach elektroluminescencyjnych, *Zeszyty Naukowe Politechniki Krakowskiej, Podstawowe Nauki Techniczne*, 2001, No. 33.

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