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New generation of cationically UV-cured epoxy adhesives containing dyes

RAPID COMMUNICATION

Summary — A new class of cationically UV-cured epoxy resin base adhesives containing dyes and allyl or 1-propenyl ether modifiers has been elaborated. The dyes (commercial product of Ciba) were directly applied into the systems and showed very good solubility in compositions studied. Model ethers containing OH groups, *i.e.* monoallyl or mono-1-propenyl ether of butane-1,4-diol (MoAlE and MoPnE, respectively) have been chosen as modifiers. The effects of the type of dye on UV-reflection, adhesion to glass and the shear strength have been determined. The obtained adhesives were intensively colored, transparent, and characterized by very good adhesion to glass and high cohesion at room temperature.
Key words: epoxy adhesives, dyes, plastifying modifiers, cationic UV-curing, adhesion to glass.

UV-radiation curing has become a well accepted technology which, because of its distinct advantages, has found manifold industrial applications, mainly for fast-drying protective coatings, printing inks and adhesives. A solvent-free liquid resin can be transformed almost instantly into a solid polymer material simply by exposure to UV light at ambient temperature, without emission of volatile organic compounds [1—3]. UV-curing technology of epoxy resins has showed rapid commercial growth within the last 10—20 years. It seems to be very attractive from both chemical and economical points of view. UV-cured epoxy polymers show many useful properties (*i.e.* excellent adhesion, good chemical resistance and good mechanical properties) but, in general, are not satisfactory in respect of toughness and embrittlement. The flexibility and other properties of the resulting polymers can be adjusted by the choice of flexibility granting crosslinking agents. Recently, there have been many approaches to modifying of the formulation of epoxy systems with the aim to improve the toughness [4].

Our previous researches have demonstrated that the most effective modifiers of epoxy bisphenol A-based resin are multifunctional allyl or prop-1-enyl ethers of selected diols. It was also concluded that allyl or prop-1-enyl ethers containing unprotected primary OH groups were especially reactive and could be included into a new class of the monomers active in cationic polymerization (called monofers) [5—7]. It was demonstrated that the introduction of these ethers to the epoxy resins caused appreciable drop in T_g and simultaneously improved flexibility of UV-cured epoxy polymers (plastifying effect).

The epoxy resins are characterized by a good wetting power of solid substrate although a proper dispersion of organic pigment or dye in a resin can be difficult to achieve. Thus, the coloration of epoxy resin is relatively complicated. The use of dyes as colorants in photoreactive systems shows no negative influence on the crosslinking process initiated by UV light. The dyes exhibit very high extinction coefficients (absorption), thus relatively low dye concentrations are sufficient to obtain the intensively colored films [8].

In this paper we present a new class of UV-cationically crosslinked epoxy resin base-adhesives including commercially available dyes and model allyl or prop-1-enyl ether (AlE or PnE, respectively) as UV-reactive modifiers (Mo). The allyl or prop-1-enyl ether of 1,4-dihydroxybutane containing primary OH group, *i.e.* 4-allyloxybutane-1-ol (MoAlE) [Formula (I)] or 4-(prop-1-enyl)oxybutane-1-ol (MoPnE) [Formula (II)] were used. To our best knowledge, in literature there are no other reports on the UV-cured colored epoxy resin based adhe-

$$CH_2{=}CH-CH_2-O-(CH_2)_4-OH \qquad (I)$$

$$CH_3-CH{=}CH-O-(CH_2)_4-OH \qquad (II)$$

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sives. Besides the technological novelty which an introduction of the dyes to the systems discussed forms, we have investigated also the dyes effects on the adhesive characteristics of the joints obtained.

EXPERIMENTAL

Materials

The epoxy bisphenol A-based resin Epidian 6 was purchased from Z. Ch. Nowa Sarzyna (Poland). The modifiers — monoallyl and mono-prop-1-enyl ethers of butane-1,4-diol were prepared as described previously [9, 10].

The cationic photoinitiator (*CPI*) — triarylosulfonium salts with SbF_6^- anion (as 50 % solution in propylene carbonate), supplied by Aldrich Chemical Co., Germany, was used.

The adhesives were colored by selected dyes, *i.e.* Microlith Red 2G-A, Microlith Green G-A, Microlith Blue 4G-A, Microlith Black 3G-A, supplied by Ciba (Germany).

Preparation of colored epoxy adhesives

Compositions of epoxy resin/monoether/cationic initiator/dye, used at optimal (100/10/1/1) weight ratio, were prepared. The dyes were initially dissolved in MoAlE or MoPnE and the obtained mixtures were incorporated into the adhesive formulations. As manual stirring appeared to be sufficient to achieve good homogenization of all components. Prior dissolving of the dyes in monoethers appeared to be necessary as manual stirring of all the components simultaneously led to heterogeneous systems' formation. The used weight ratio of the components was selected on the basis of previous studies [5].

Curing of adhesives

The photoinitiated polymerization (radiation curing) of prepared compositions was conducted between two glass plates (thickness of the layer corresponded with laying on 30 g onto m^2) under 450 W arc lamp. Irradiation (λ = 315—400 nm) was performed at room temperature, in air atmosphere, during 5 min. As the results, the transparent, intensively colored and crosslinked solid polymer joints were obtained.

Methods

UV-reflection measurements were performed using Gretag-Macbech spectrometer (Germany). Shear strength and adhesion were determined using Zwick PC-Softwer Z7005 testing machine (Germany) according to AFERA 4001 (adhesion) and AFERA 4012 (shear strength).

RESULTS AND DISCUSSION

In the preliminary studies, we have found that the introduction of MoAlE or MoPnE as plastifying modifiers (in a range of amounts 3—15 wt. %) into Epidian 6 resin did not deteriorate other physical and mechanical properties of final adhesive products. We have also observed that the presence of dyes (in amount of 1 wt. %) in studied UV-cured systems had no negative influence on their useful properties. In the further researches the previously mentioned optimal weight ratio of resin/monoether/initiator/dye (100/10/1/1) was established.

Significant advantages of the described crosslinking process are, characterized already in experimental part, its conditions *i.e.* very short irradiation time at room temperature and in the air atmosphere. The colored adhesives of good quality with very good adhesion to glass were achieved (Fig. 1), though in the case of Microlith Black 3G-A dye, a nearly 2.5-fold reduction in value of adhesion was noted in comparison with uncolored adhesive. But also adhesion value of this dye matches the range acceptable for the industry (≥180 N/2.5 cm).

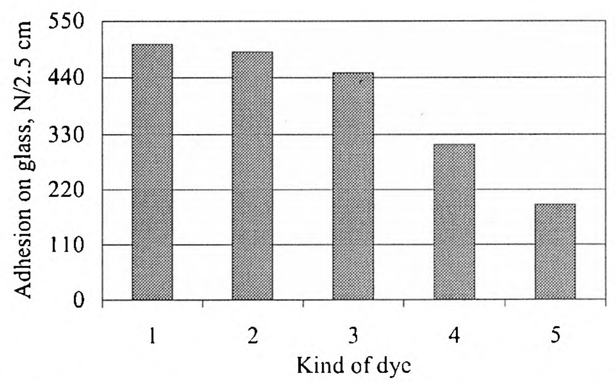

Fig. 1. Effect of kind of dye on adhesion to glass of Epidian 6/MoAlE/CPI/dye compositions (100/10/1/1): 1 — no dye, 2 — Microlith Blue 4G-A, 3 — Microlith Green G-A, 4 — Microlith Red 2G-A, 5 — Microlith Black 3G-A

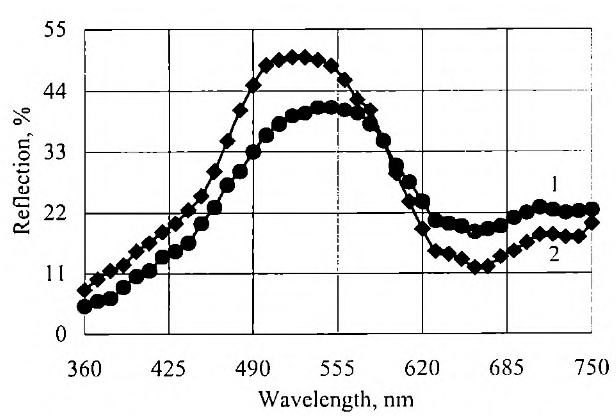

Fig. 2. Effect of MoPnE (1) and MoAlE (2) on UV-reflection values of Epidian 6/monoether/CPI/Microlith Green G-A composition (100/10/1/1)

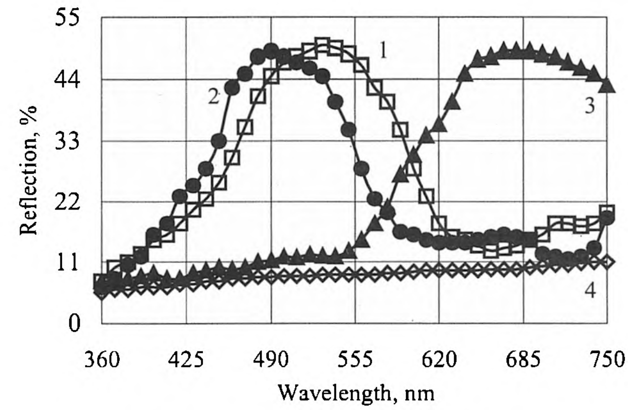

Fig. 3. Effect of kind of dye on UV-reflection values of Epidian 6/MoAlE/CPI/dye compositions (100/10/1/1): 1 — Microlith Blue 4G-A, 2 — Microlith Green G-A, 3 — Microlith Red 2G-A, 4 — Microlith Black 3G-A

The maximum values of UV-reflection of the obtained joints modified by MoAlE or MoPnE with Microlith Green G-A as a dye are equal about 50 % or 40 %, respectively (Fig. 2). However, the UV-reflection values was lower in the case of MoPnE modifier than MoAlE one. It could be connected with higher reactivity of prop-1-enyl ether monomer in the cationically initiated photopolymerization process [4, 5]. Figure 3 is illustrative of the kind of dye on reflection values of our adhesives. Blue, Green or Red dyes nearly do not differ in maximal value of this property, they just differ in maxima positions on the wavelength axis. Black dye significantly differs from this group. But, as it results from the industrial practice, in spite of different courses of the curves presented in Fig. 3, all the dyes investigated can be successfully used for preparation of colored, radiation cured epoxy resins based adhesives.

Table 1. Shear strength of uncolored and colored epoxy adhesives Epidian 6/MoAlE/CPI/dye, measured after UV crosslinking

	Kind of dye				
	Dye free	Microlith Blue 4G-A	Microlith Green G-A	Microlith Red 2G-A	Microlith Black 3G-A
Shear strength, N	300	313	326	340	371

Shear strength, being a criterion of evaluation of adhesion to glass, is a very important property, describing the quality of adhesive systems. Data presented in Table 1 show the effects of the presence and type of a dye on shear strength. So, the introduction of dyes into the epoxy/monoether/initiator compositions improves shear strength.

On the basis of shear strength and UV-reflection investigations we concluded that the introduction of dyes to the compositions improved ability of UV absorption during the polymerization, and what followed — increased reactivities of these systems in the process. The adhesives obtained show very good adhesion and cohesion parameters, especially when Microlith Black 3G-A dye is used (6 % of UV-reflection = 370—750 nm, shear strength = 371 N), and are characterized by transparency and intensive color. The lower UV-reflection of the dyes used, the higher shear strength of examined epoxy adhesives systems after UV-curing.

As expected, an increase in shear strength (Table 1) and a decrease in adhesion to glass (Fig. 1) of epoxy adhesives containing diverse dyes correspond to the reflection level in the radiation area and to the maxima of reflection for dyes evaluated (Fig. 3).

So the results of evaluation of the dyes effects on the coating properties, based on adhesion investigations (shear strength) and reflection measurements, fit in each with other. Data presented in this paper let state that new, colored, transparent epoxy resins based adhesives we developed are suitable for advantageous use in glazier's industry.

REFERENCES

1. Masson F., Decker C., Jaworek T., Schwalm R.: *Progr. Org. Coat.* 2000, **39**, 115.
2. Allen N. S.: *J. Photochem. Photobiol. A: Chem.* 1996, **100**, 101.
3. Crivello J. V., Jo K.: *J. Polym. Sci., Part A: Polym. Chem.* 1993, **31**, 1483.
4. Day R. J., Lovell P. A., Wazzan A. A.: *Polym. Int.* 2001, **50**, 849.
5. Martysz D., Antoszczyszyn M., Urbala M., Krompiec S., Fabrycy E.: *Prog. Org. Coat.* 2003, **46**, 302.
6. Martysz D., Urbala M., Antoszczyszyn M., Pilawka R.: *Polimery* 2002, **47**, 849.
7. Martysz D., Antoszczyszyn M.: *Przem. Chem.* 2003, **82**, 921.
8. Czech Z.: "Vernetzung von Haftklebstoffen auf Polyacrylatbasis", Wyd. Politechniki Szczecińskiej, Szczecin 1999.
9. Janus E., Antoszczyszyn M., Urbala M.: *Polish J. Appl. Chem.* 1999, **43**, 77.
10. Urbala M., Antoszczyszyn M., Krompiec S.: *Polish J. Chem. Tech.* 2001, **3**, 22.

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