

INVESTIGATION OF EMULSIFIED HYDROUS EPOXY SYSTEMS

UDC 691.16

Saša Zlatković¹, Ljiljana Rašković²,
Goran Nikolić³, Jakov Stamenković³

¹Pharmaceutical & Chemical Industry "Zdravlje-Pharmaco", Leskovac, 199 Vljakova St.

²Dyes and Lacquers Industry "Pomoravlje" Niš, 129 Bulevar 12. februar

³Faculty of Technology, Leskovac, 124 Bulevar oslobodjenja

Abstract. *The hard resin was dispersed in water EP 384 W (Solutia-Vianova, Austria) and cross-linked with aliphatic polyaminaduct hardener EH 623 W (Solutia-Vianova, Austria) and distilled water in a stoichiometric ratio of 50:10:20, respectively. The degree of the epoxy resin cross-linking and the quantity of unreacted epoxy groups have been monitored by the FTIR spectroscopic method. The optimal time of total cross-linking as the measure of the degree of cross-linking was determined by indirect measuring of the film hardness (JUS.H.C8.055).*

Key Words: *Epoxy system, degree of cross-linking, FTIR spectroscopic method, film hardness*

INTRODUCTION

As a consequence of legal restrictions in terms of utilization of organic solvents in coating products and as an answer to current health, safety and ecological requirements, the systems based on water emulsions of epoxy resins and hardeners are used more and more.

In practice, there is a need for water binders in the form of coatings which would be applied in specified working conditions and which would have to possess the good ability of film forming at the ambient temperature without need for additional solvent, to have good working characteristics and attractive flexibility [1].

Two-component epoxy coating systems, which neither contain easily evaporable organic content nor an emulsifier, have thus been developed and an emulsion of epoxy resin with a low MFT (minimal film forming temperature) which is compatible with the whole range of hydroxy epoxy hardeners, has been obtained.

An epoxy resins emulsion has extraordinary emulsifying characteristics which enable incorporation of low-viscous hardeners containing polyamines, and all that in water as a medium.

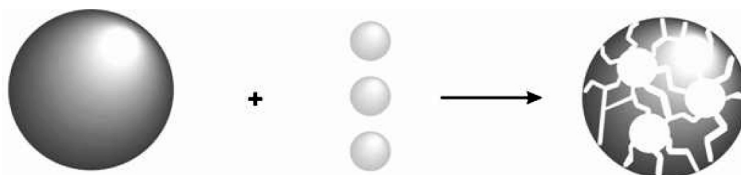


Fig. 1. Schematic presentation of resin/hardener reaction in the medium of water

Reaction increases

- molecular mass
- temperature of transition into glass (T_g)
- minimal film forming temperature
- resistance to deformation

The hard resin particle size in water dispersion is about 500 nm [2]. Reaction with the hardeners starts from the surface of the resin particles and ends near the center of the particle, and about 80% of the epoxy resin quantity in the particle will be cross-linked by the end of the reaction (Figure 1) [3].

For the purpose of environmental protection, in the production of epoxy resins emphasis is placed on the emulsions of epoxy resins and hardeners in water solutions so as to avoid the toxic effect of the organic solvents. For that purpose, modified polyamidoamines are used not only as hardeners, but also as emulsifiers.

The choice of a particular cross-linking agent depends on the applied technique, required potlife, cross-linking conditions and wanted characteristics.

Hardeners can be described as being hydrophylic and less hydrophylic (soluble and less soluble in water). This refers to whether amino groups in amino segments of the hardeners are bound to both the primary and the secondary carbon atoms or only to the secondary ones, because they show difference in reactivity. The cross-linking agents in which the NH_2 -groups are bound to the secondary carbon atom show lesser reactivity.

During the making of the colorless hydrous coatings, the following parameters are important: potlife, knitting of wet film and drying, hardness, resistance to dissolving and resistance to forming a spot of water. The potlife of these products ranges from 1, 5 to a maximum 3 hours. It is determined through an increase in viscosity, especially in the systems with a hydrophylic hardener, or through clarity, i.e. loss of film shine which is monitored on the glass plate.

THE EXPERIMENT

The epoxy resin cross-linking was carried out at room temperature [4]. The specified quantities of epoxy resin EP 384 W, hardener EH 623 W and distilled water were subjected to mixing in a stoichiometric ratio of 50:10:20 respectively. The obtained mixture was applied to a hard base. The films were formed at ambient temperature by the reaction of polyaddition [5].

The hardness of the dry film was determined indirectly (standard JUS.H.C8.055), by measuring the time during which the oscillating amplitude of the specified pendulum lying on the film was reduced [6].

The process of epoxy resin cross-linking with the chosen hardener was monitored by IR spectroscopy [7]. The FTIR spectra of the basic epoxy resin and the hardener were recorded by a method of applying thin film on the carrier KRS-5 plates, and the FTIR spectra of the cross-linked resin were recorded by means of the KBr technique [8]. The recordings were carried out on the spectroscope Bomem Hartmann&Braun MB-100 series, in the range of wave numbers 4000-400 cm^{-1} at a resolution of 2 cm^{-1} . The original Win-Bomem&Easy software was used to determine the areas of the characteristic bands.

Validation of the IR test results was carried out by a chemical method (JUS.G.S1.811) [9].

RESULTS AND THE DISCUSSION

The epoxy resin EP 384 W, which is by composition a hard resin dispersed in water (composition 53% hard, 40% water and 7% methoxy propanol) was used in the investigation. Technical characteristics of epoxy resin EP 384 W are shown in Table 1.

Table 1. The physical and chemical characteristics of the epoxy resin EP384W

Resin mark	Composition	η_{25} (mPas)	Epoxy number (Eq/g)	Epoxy equivalent (g/Eq)	Flash point ($^{\circ}\text{C}$)
EP384W	Hard resin, Dispersed in water 53% hard 40% water 7% methoxypropanol	350-650	1.81-2.04	490-550	≥ 100

Epoxy resin EP 384 W was cross-linked with the hardener EH 623 W, whose characteristic parameters are shown in Table 2.

Table 2. The physical and chemical characteristics of the applied hardeners EH623W

Hardener mark.	Composition	η_{23} (mPas)	H-activ. equivalent (g/Eq)	Flash point ($^{\circ}\text{C}$)
EH623W	Aliphatic polyaminaduct	12.000-21.000	160	≥ 100

Change of film hardness was determined for a stoichiometric ratio of EP 384 W: EH 623 W: H₂O = 50:10:20, that is, the epoxy resin system 1 V and the values are shown in Table 3.

Table 3. The change of film hardness by cross-linking of the epoxy system 1V

Days	1	2	3	4	7	9	10	14	15
Hardness (sec Kō)	87	106	134	169	175	183	188	190	190

By analyzing the obtained results it can be observed that the degree of hardness reaches a constant value in the period after the 14th day, which points out that the cross-linking process in this system was completed after the 14th day.

DETERMINATION OF THE CONTENT OF THE EPOXY GROUP
BY THE SPECTROSCOPIC METHOD

The characteristic epoxy group in the investigated epoxy resin EP 384 W can be identified [10] on the basis of band presence in the IR spectrum $3060\text{--}3000\text{ cm}^{-1}$ from a valent CH vibration of the epoxy ring (ν_{CH}), 1250 cm^{-1} , from valent CO vibrations of the epoxy ring (ν_{CO}) and at $960\text{--}810\text{ cm}^{-1}$ from the deformed CH vibrations of the epoxy ring (γ_{CH}). For a more detailed analysis, that in a valent IR range there is a band with a centroid at 3036 cm^{-1} originating from CH vibration of the aromatic ring should be kept in mind.

The reduction of intensity and the almost complete disappearance of the IR band at 3056 cm^{-1} in the cross-linked water system IV, is characteristic of an epoxy ring opening, its reactivity and contents change. This fact gives the possibility of quantitative determinations of the reacting epoxy groups during the cross-linking, i.e. the degree of resin cross-linking. In favor of this cross-linking mechanism (addition of hydrogen from hardener's amino group to the epoxy resin), speaks of the change in intensity and band position of the newly formed OH group in the valent IR range at about $3417\text{--}3433\text{ cm}^{-1}$, depending on the day of cross-linking and the band's intensity change in the range of $1150\text{--}1050\text{ cm}^{-1}$ from ν_{CO} and ν_{CC} vibration, and in the range of $960\text{--}850\text{ cm}^{-1}$ from γ_{CH} vibration.

The calibration diagram of the epoxy group content (from epichlorohydrin) vs. the area of the characteristic IR band of the epoxy group was constructed for the purpose of an exact determination of quantitative change of the epoxy group in a cross-linked system I V.

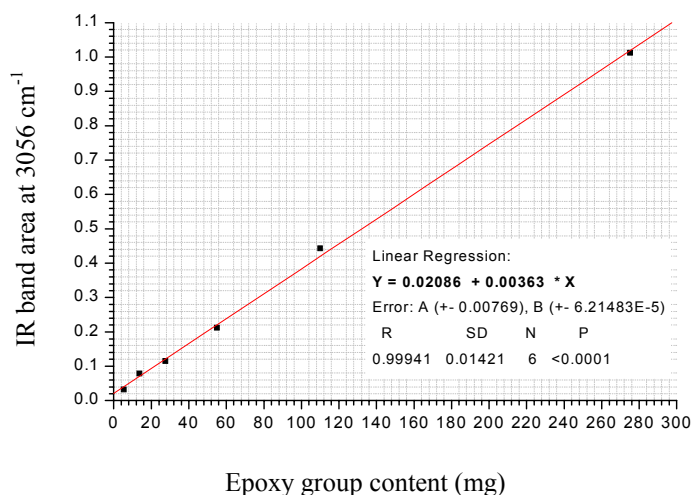


Fig. 2. The calibration diagram of the epoxy group's content in the function of the area of the characteristic IR band at 3056 cm^{-1}

The reading of the total area of the band consisting of two absorption maxima in the range of $3080\text{--}3020\text{ cm}^{-1}$ was done from the recorded FTIR spectra of the cross-linked system IV, by means of the original Win-Bomem& Easy software [11]. As this band is formed by overlapping the bands of the reacting epoxy group (ν_{CH} at 3056 cm^{-1}) and the

unsaturated aromatic ring (ν_{CH} at 3038 cm^{-1}) it was not possible to perform a precise separation. Having in mind that aromatic group's content does not change during the cross-linking, the share of the epoxy group area (P1, Figure 3) was determined by the mathematical method of square covering [12], whereby the percentage share of the individual bands in relation to the IR band total area is calculated.

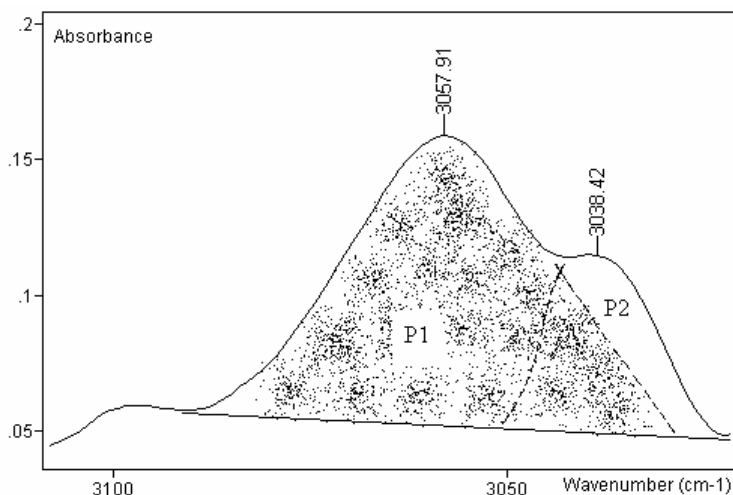


Fig. 3. The FTIR Spectrum of the non-cross-linked resin EP384W in the valent CH range $3100\text{-}3000 \text{ cm}^{-1}$. The hatched area P1 represents the area of the epoxy group peak and P2 represents the area of the aromatic ring peak.

The IR peak area change, corresponding to the content of the unreacted epoxy group in the cross-linking process, is shown in the function of cross-linking time in Fig. 4.

From the results obtained by measuring the characteristic IR band area (Fig. 4) and by means of a calibration diagram (Figure 2), the remaining content of epoxy groups in the cross-linking process in the water system 1V with time, which at the same time represents the measure of the cross-linking degree (Table 4), was determined. On the basis of the content of the unreacted epoxy group in the cross-linking process being $23,8 \text{ mg}$ in the mass of epoxy resin of $2,0 \text{ g}$, the maximum cross-linking degree of $75,3\%$ after 14 days for the initial given stoichiometric ratio $50:10:20$ (EP 384 W: EH 623 W: H_2O) was determined.

The validity of the developed FTIR method during work was checked by the standard chemical method for epoxy group content determination, that is, the epoxy equivalent. By comparison of the obtained results of the epoxy group's content by the chemical and spectroscopic method (Table 4), an exceptionally good agreement of the results with the margin for error being less than 3% , can be observed.

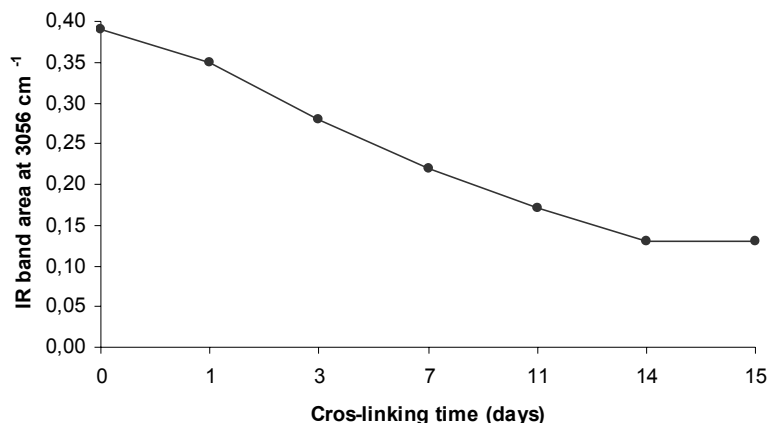


Fig. 4. The diagram of the change of the area of the IR band of the epoxy group in the function of time of the system 1V cross-linking.

Table 4. The content of the epoxy groups and the degree of cross-linking of the epoxy system 1V with time

Time (days)	0	1	3	7	11	14	15
Content of the epoxy group, by the chemical method (mg)	96,75	89,1	69,1	60,2	31,5	24,2	24,2
Content of the epoxy group, by the spectroscopic method (mg)	95,50	88,2	68,4	59,4	30,6	23,8	23,8
Degree of cross-linking of the resin, by the spectroscopic method (%)	0	8,8	29,3	38,6	68,3	75,3	75,3

By comparing the results for the degree of film hardness (Table 4), with the results of the cross-linking degree, it can be observed that the cross-linking process was in both cases completed after the 14th day.

CONCLUSION

- By indirectly measuring the film hardness, the optimal stoichiometric ratio of the components was determined to be 50:10:20 in the process of a two-component system forming.
- The optimal time for total cross-linking of the epoxy system of 14 days was determined, after which the system can be practically applied.
- The FTIR spectroscopy proved to be a good method for monitoring and assigning characteristic changes which occur during the process of an epoxy system cross-linking.
- The method of the FTIR spectroscopy was developed to determine the degree of epoxy resin cross-linking and the quantity of the unreacted epoxy groups. With this method the results are obtained with the margin for error being less than 3%, in comparison with the standard chemical method.

– On the basis of the content of the unreacted epoxy group in the cross-linking process being 20, 8 mg in the epoxy resin mass, the maximum degree of 75, 3% of cross-linking was determined after a specified period of time and for the initially given stoichiometric ratio.

– By correlation of the FTIR spectra and parameters which directly depend on the degree of cross-linking, as well as the time of applicability of the epoxy resins, the optimal stoichiometric ratio of the components can be defined, as a prerequisite for the forming of the two-component epoxy system of relatively higher elasticity, adhesivity and water-proofing.

REFERENCES

1. Lj.Rašković, The basis of polymeric engineering, Faculty of technology, Leskovac, 26-33. , 1995.
2. Lj.Rašković, S.Zlatković, Collection of papers, 18.th Symposium on corrosion and material protection, Belgrade, 43-54., 2002.
3. Ciba Geigy Publ.№28337/e, Basel, Switzerland, 1989.
4. Lj.Rašković, S.Zlatković, Sbornik naučnih trudov, Meždunarodnaja naučno-metodičeskaja konferencija, Rossijskaja Federacija, Belgorod, 140-151.,2003.
5. Ciba Geigy Publ.№28316/2/e, Basel, Switzerland, 1991.
6. JUS Standard, H.C8.055. Federal Institution for standardization, Belgrade, 1994.
7. S.Zlatković, G.Nikolić, J.Stamenković, Determination of the cross-linking degree of unmodified epoxy resin by cycloaliphatic polyamine and polyamidamin hardeners by FTIR spectroscopy, *Chem.Ind.* , 57 , (11) (563-567) (2003).
8. Graseby Specac, Sampling techniques for infrared analysis, USA, 1997.
9. JUS Standard G.S1.811. Federal Institution for standardization, Belgrade, 1990.
10. S.Milosavljević, Struktural instrumental methods, Faculty of chemistry, Belgrade, 49-132., 1994.
11. Bommem Hartmann&Braun, The Michelson series FTIR spectrometer, Users guide, Quebec, Canada, 85-104., 1994.
12. N.Poljski, Encyclopedia of elementary mathematics, I part, Institute for textbooks publishing, Belgrade, 63-69., 1968. (Translated by O.Mitrinović).

ISPITIVANJE EMULGOVANIH VODENIH EPOKSI SISTEMA

**Saša Zlatković, Ljiljana Rašković,
Goran Nikolić, Jakov Stamenković**

Čvrsta smola dispergovana u vodi EP384W (Solutia-Vianova, Austrija), umrežavana je alifatičnim poliaminoadukt umreživačem EH623W (Solutia-Vianova, Austrija) i destilovanom vodom, u stehiometrijskom odnosu 50 : 10 : 20.

Stepen umreženosti epoksi smole i kvantitet neprereagovanih epoksi grupa praćeni su metodom FTIR spektroskopije. Optimalno vreme potpunog umrežavanja, kao mera stepena umreženosti, određivano je merenjem tvrdoće filma indirektnim putem (JUS.H.C8.055).

Ključne reči: *Epoksi sistem, stepen umreženosti, FTIR spektroskopija, tvrdoća filma*