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Studies on activity of *s*-triazine ring containing amine modifiers in curing of unsaturated polyester resins

Summary — The results of the study on the activity of amine modifiers for unsaturated polyester resins obtained by reaction of diethanolamine (3-aza-pentane-1,5-diol) and *N*-phenyl-2-aminoethanol with 2,4-dichloro-6-methoxy-1,3,5-triazine, 2-chloro-4,6-dimethoxy-1,3,5-triazine or with cyanuric chloride are presented. Effects of the type and amount of amine modifier as well as cobalt accelerator on gelation time and stability of the resins were investigated.

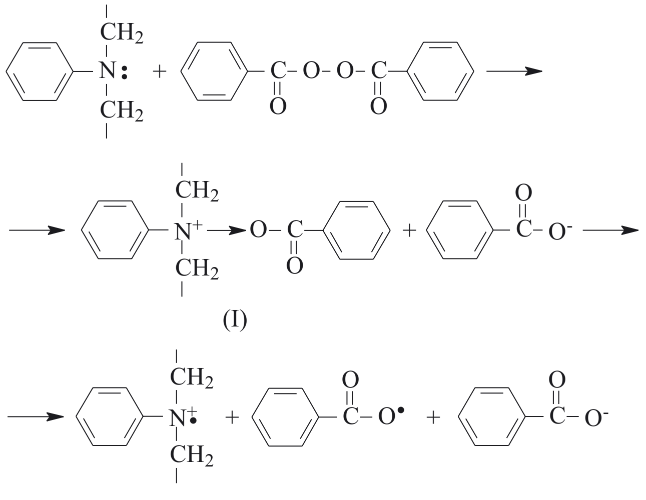
Key words: tertiary amines, unsaturated polyester resins, built-in modifiers, gelation time, stability, thermal decomposition.

AMINE CURING SYSTEM FOR UNSATURATED POLYESTER RESINS

Unsaturated polyester (UP) resins are usually cured in the system consisting of the resin itself, *i.e.*, styrene solution of UP resin and radicals producing initiator, such as benzoyl peroxide or ketone peroxides. Some compounds reduce the activation energy of peroxide decomposition and hence make possible low-temperature initiation of the curing system. These accelerators can selectively react with certain groups of initiators. In low-temperature curing of UP resins, cobalt or vanadium salts as well as tertiary amines are most often used. In the presence of cobalt salts, the curing takes place at 20 to 100 °C when 1—12 wt. % solutions of cobalt(II) octanoate or naphthenate is used [1]. Manganese accelerators with ketone peroxides yield UP resins compositions of long storage time, but cured quickly at higher temperature *i.e.* 60—100 °C, while vanadium accelerators are used for fast room temperature curing (*ca.* 20—25 °C) [1].

Tertiary amines are use in UP resins compositions with benzoyl peroxide for room-temperature curing [2]. The most widely reported industrial formulations are three-component systems consisting of polyester dissolved in styrene, peroxy initiator, and a tertiary amine [3—9]. These compositions are very reactive even at temperature as low as 5 °C [1]. The system: benzoyl peroxide/amine is often mentioned as amine-curing system of UP.

Among the amines, the most frequently used are aromatic ones, such as *N*,*N*-dimethylaniline, *N*,*N*-diethylaniline, *N*,*N*-dibutylaniline, *N*,*N*-dimethyl-*p*-toluidine, or generally, *N*,*N*-dialkylanilines. They can be dissolved in the resin component not necessarily just prior to use. Unfortunately, UP resins with dissolved amines show very poor stability. Somewhat better stability show the formulations where amine is chemically incorporated into polyester chains, already at the stage of its synthesis. So, the activator is very uniformly distributed in the bulk. This is possible when the amine has two functional groups capable of reacting with carboxylic acids (or acid anhydrides) or with diols. The easiest solution is when amine contains hydroxyl groups [10—13]. Incorporation of such an amine into resin structure may significantly accelerate gelation of the resin because of formation of active $RO^\bullet$ radicals that initiate polymerization [equation (1)] [14]:

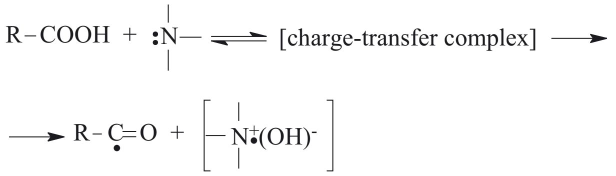


(I)

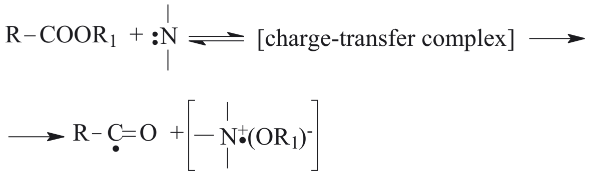
(II) (III) (1)

Initiating complex [Formula (I)] is formed in the first stage from amine and benzoyl peroxide. The complex then decomposes to a cation radical [Formula (II)] and benzoyl radical [Formula (III)] [15].

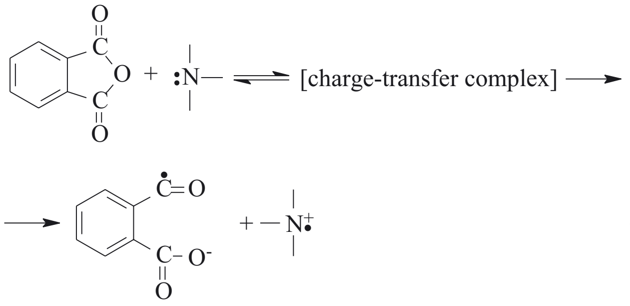
The function of *N,N*-dimethylaniline as curing preaccelerator of UP resins was described by Kłosowska-Wołkowicz, *et. al.* [16]. They found that at elevated temperature (up to 100 °C) *N,N*-dimethylaniline causes gelation of the resin even in the absence of benzoyl peroxide. The authors [16] measured gelation time for resins of various compositions. Gelation process was found to proceed through formation of dimethylamine complexes in reactions with carboxylic acid, ester, or anhydride groups [equation (2)—(4), respectively]; those complexes decomposed at elevated temperature to yield the radicals initiating polymerization.



$$R{-}COOH + :\overset{|}{\underset{|}{N}}{-} \rightleftharpoons [\text{charge-transfer complex}] \longrightarrow R{-}\dot{C}{=}O + \left[-\overset{|}{\underset{|}{N}}{}^{+\bullet}(OH)^{-}\right] \quad (2)$$



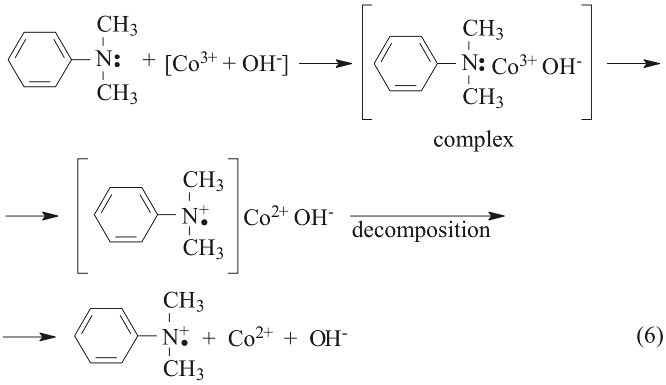
$$R{-}COOR_1 + :\overset{|}{\underset{|}{N}} \rightleftharpoons [\text{charge-transfer complex}] \longrightarrow R{-}\dot{C}{=}O + \left[-\overset{|}{\underset{|}{N}}{}^{+\bullet}(OR_1)^{-}\right] \quad (3)$$



(4)

UP resins are very frequently cured with the use of metal containing accelerators of hydroperoxide decomposition. The most popular is cobalt(II) naphthenate added in the amount of 0.002—0.03 wt. % [17]. The systems containing these components are often mentioned as cobalt-curing ones. The most effective accelerating systems consist of metal and amine both built into polyester structure [18, 19]. The promoting effect of amine incorporated either chemically or physically to UP resins in the cobalt-curing system has been explained by Jada [18] and Kharash [19], what is shown in equations (5) and (6), where ROOH is a hydroperoxide.

$$Co^{2+} + ROOH \longrightarrow Co^{3+} + RO^{\bullet} + OH^{-} \qquad (5)$$



(6)

As it was mentioned in [18, 19], amine does not act just by complexing Co^{3+} and its reduction to Co^{2+}, but it can initiate decomposition of hydroperoxide. Hence, introduction of cobalt(II) salt to UP resin modified with aromatic tertiary amine containing reactive hydroxyl groups results in a substantial reduction of gelation time. Cobalt(III) ions formed in the reaction of hydroperoxide with Co^{2+} are first complexed and then reduced thus leading to formation of active $RO^{\bullet}$ radicals that initiate the curing. Also amine itself can decompose hydroperoxide and add up to the curing process [18, 19].

Quarternary ammonium salts are added in order to improve storage stability of UP resins. Their effect can be explained in terms of reduced rate of ageing of UP resins due to capture of $RO^{\bullet}$ radicals.

The aim of this work was the investigation of novel tertiary amines that can be used as modifiers for UP resins. They are prepared in reactions of 2,4-dichloro-6-methoxy-1,3,5-triazine or 2-chloro-4,6-dimethoxy-1,3,5-triazine with diethanolamine (3-azapentane-1,5-diol) and *N*-phenyl-2-aminoethanol and in reactions of cyanuric chloride with diethanolamine and *N*-phenyl-2-aminoethanol. Preliminary results of a study of their effects on gelation behavior and stability of unsaturated polyester resins are also reported.

EXPERIMENTAL

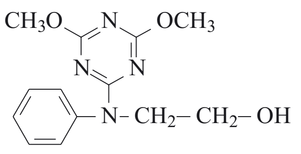
Materials

Unsaturated polyester resins were obtained from the following reagents (used without purification): phthalic and maleic anhydrides (Nitrogen Works, Kędzierzyn SA, Poland), 3-oxapentanone-1,5-diol (diethylene glycol) and propane-1,2-diol (propylene glycol) (both produced by Polish Petroleum Concern Orlen SA, Płock).

The modifiers denoted as A—F of the following formulae were used.

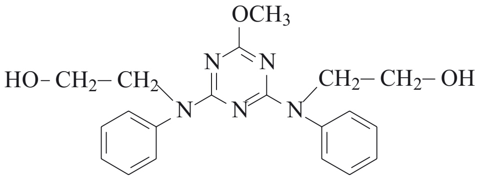
All of them have *s*-triazine ring in their structures. They contain one, two or three *N*-phenyl-*N*-(2-hydroxyethyl) groups (modifiers A—C) or *N,N*-bis(2-hydroxyethyl) groups (modifiers D—E) linked to *s*-triazine ring.

Benzoyl peroxide (Interox GZ-S, 50 % paste in dibutyl phthalate, Peroxid-Chemie GmbH, Germany) was used as a typical curing agent.



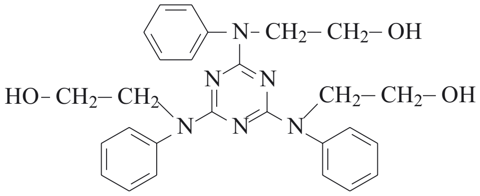
modifier **A**

2-[*N*-phenyl-(2-hydroxyethyl)amine]-4,6-dimethoxy-1,3,5-triazine



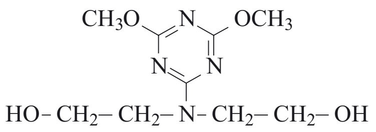
modifier **B**

2,4-bis[*N*-phenyl-(2-hydroxyethyl)amine]-6-methoxy-1,3,5-triazine



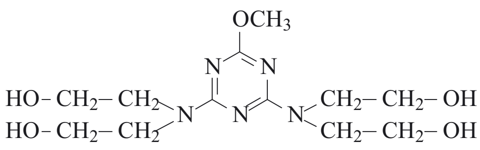
modifier **C**

2,4,6-tris[*N*-phenyl-(2-hydroxyethyl)amine]-1,3,5-triazine



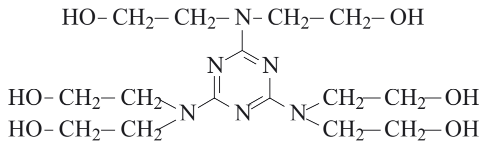
modifier **D**

2-[*N*,*N*-bis(2-hydroxyethyl)amine]-4,6-dimethoxy-1,3,5-triazine



modifier **E**

2,4-bis-[*N*,*N*-bis(2-hydroxyethyl)amine]-6-methoxy-1,3,5-triazine



modifier **F**

2,4,6-tris-[*N*,*N*-bis(2-hydroxyethyl)amine]-1,3,5-triazine

The standard cobalt-curing initiating system Luperox K-1 (Atochem Chemie GmbH, Germany) consisting of cobalt(II) octanoate as accelerator and butanone peroxide dissolved in dibutyl phthalate was utilized.

Preparation of modifiers

The syntheses of 2-chloro-4,6-dimethoxy-1,3,5-triazine, 2,4-dichloro-6-methoxy-1,3,5-triazine as well as D, E and F modifiers were described in [20].

Detailed description of the syntheses of A, B and C modifiers were described in [21].

Syntheses of modified unsaturated polyester resins

To a three-necked 500 cm^3 flask equipped with a mechanical stirrer, inlet for inert gas (nitrogen), thermometer, Liebig condenser and calibrated distillate collector, 76.1 g (0.5 mole) of phthalic anhydride, 49.0 g (0.5 mole) of maleic anhydride, 41.0 g (0.43 mole) of diethylene glycol, 42—44 cm^3 (0.57—0.60 mole) of propylene glycol (depending on the amount of amine-glycol modifier added), and the modifier itself up to 6.4 g (2.0 wt. % with respect to the total mass of all substrates) were introduced. The flask was run-purged with nitrogen for 15 min before heating was switched on. Then 0.18 cm^3 (*ca.* 12 mg) of 10 % solution of hydroquinone in acetone was added and the content was heated at 165—200 °C under nitrogen for 9—12 h, until the acid number of the mixture has dropped down to below 50 mg KOH/g of resin. The mixture was then cooled down to 90—100 °C and diluted with 125 cm^3 of styrene stabilized with hydroquinone.

Curing of modified resins

The recommended amount of initiator, 0.5 g initiator/25.0 g resin, or over-standard amount of initiator, 1.0 and 1.5 g initiator/25 g resin, were used in the experiment. For both the standard and over-standard amounts of initiator, the following amounts of cobalt accelerator solution were added: 0.10, 0.15, 0.25 or 0.50 cm^3 (to react with 0.5, 1.0 or 1.5 g initiator per 25 g of resin). The rate of curing was measured.

Analytical methods

Polycondensation

The extent of polycondensation reaction was followed by measuring the amount of water released from the system and, at the end of reaction, by measuring the acid number (*AN*). The synthesis of unsaturated polyester resin was carried out until *AN* dropped down below 50 mg KOH/g [Polish Standard PN-87/C-89082/11 (Polish version of ISO 2114-1974)].

Cured resins

By using standard procedures [Polish Standard PN-87/C-89082/15 (Polish version of ISO 2535-1974)] the time of gelation ($t_{gel.}$) at 25 °C (time until air bubble was arrested in the test tube filled with resin containing initiator) and stability of resins at 70 °C (time until air buble was arrested in the test tube filled with resin containing no initiator) — Polish Standard PN-86/C-89082/09 were determined for all unsaturated polyester resins.

The time of gelation was measured for so-called amine-curing system, *i.e.* with benzoyl peroxide as initiator, as well as for the cobalt-curing system consisting of butanone peroxide initiator and cobalt(II) octanoate accelerator. A series of curing experiments with cobalt curing system was performed with an addition of 0.3 wt. % of benzyltriethylammonium chloride.

Differential thermal analyses of the unsaturated polyester resins were made using F. Paulik, J. Paulik and L. Erdey system derivatograph (MOM, Hungary) under the following conditions of registration: sample mass 100 mg, temperature range from 20 °C to 1000 °C, nitrogen atmosphere, registration time 100 min, applications DTA 1/10, DTG 1/15.

RESULTS AND DISCUSSION

Gelation time

Gelation times for all resins modified with compounds A—F were very long. They ranged from *ca.* 120 to *ca.* 360 min. The resins containing modifiers with *N*-phenyl-*N*-(2-hydroxyethyl) groups (A—C) yielded somewhat shorter gelation times, in the range from 120 to 200 min. The more modifier was introduced to a resin, the shorter was its gelation time. On the other hand, the resins with modifiers containing *N,N*-bis(2-hydroxyethyl) groups (D—F) showed very long gelation times (170—295 min) and the relation between gelation time and modifier percentage had a form of inverted parabola with maximum around 1.0 to 1.25 wt. % of modifier built into the resin structure. Those were the reasons why further curing experiment were carried out using earlier mentioned system: modified polyester resin/cobalt accelerator/initiator (butanone peroxide "Luperox K-1").

Time of gelation at room temperature (25 °C) for the standard resin cured with butanone peroxide and with accelerator [1.0 wt. % of cobalt(II) octanoate dissolved in styrene] was not very long. Introduction of 0.25 to 2.0 wt. % of any of amine modifiers into the resin structure yielded a substantial reduction of gelation time when butanone peroxide was used.

The results of reactivity measurements along with those of storage stability are presented in Fig. 1—6.

It was observed that introduction of any modifier A—F reduces gelation time of the modified resin as compared with that of unmodified resin.

Addition of A, B or C in the range 0.25 to 2 wt. % results in $t_{gel.}$ shortening with increasing amount of modifier in the resin. The monotonic tendency remains the same regardless of whether the normative or over-standard amount of inhibitors is used (Fig. 1).

Gelation time also decreases when D, E and F modifiers are used in the same concentration range. However the relationship gelation time *vs.* modifier amount in polyester resin has here more or less the shape of a parabola with minimum at *ca.* 1.25 wt. % of modifiers built into the polyester (Fig. 2). The curves are similar for the standard or over-standard amount of initiator.

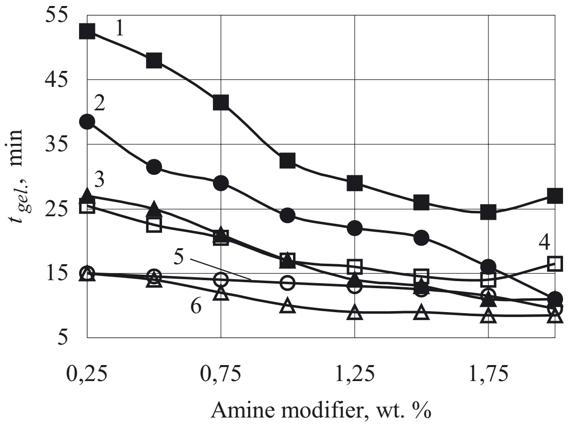


Fig. 1. Effects of kind and amount of amine modifiers on gelation time ($t_{gel.}$) of UP resins. Modifiers: A — curves 1 and 4, B — curves 2 and 5, C — curves 3 and 6; conditions of gelation: full marks — 0.1 cm^3 of cobalt accelerator and 0.5 g of initiator/25 g resin (standard) and empty marks — 0.1 cm^3 of cobalt accelerator and 0.1 g of initiator/25 g resin (over standard)

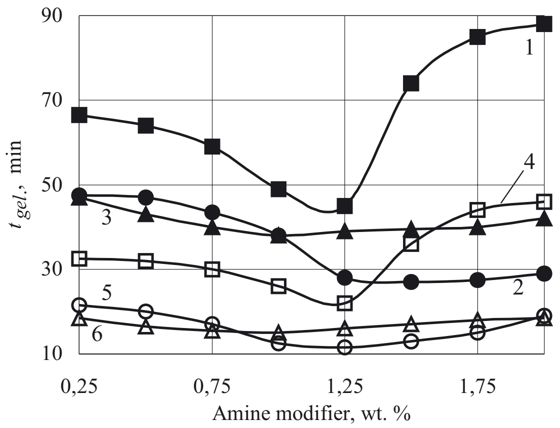


Fig. 2. Effects of kind and amount of amine modifiers on gelation time ($t_{gel.}$) of UP resins. Modifiers: D — curves 1 and 4, E — curves 2 and 5, F — curves 3 and 6; conditions of gelation: full marks — 0.1 cm^3 of cobalt accelerator and 0.5 g of initiator/25 g resin (standard) and empty marks — 0.1 cm^3 of cobalt accelerator and 0.1 g of initiator/25 g resin (over standard)

Most significant effect of increase in amount of cobalt accelerator solution on $t_{gel.}$ is observed in the range up to 0.3 cm^3 per 25 g of resin both at standard and over-standard amount of initiator. In the latter case gelation time was far shorter. This was observed for all modifiers. Further increase in cobalt(II) octanoate concentration did not reduce $t_{gel.}$, anymore (Figs. 3 and 4).

By building into unsaturated polyester resin the modifier containing *N*-phenyl-*N*-(2-hydroxyethyl) groups (A—C modifiers) or *N,N*-bis(2-hydroxyethyl) groups (D—F modifiers), gelation time gradually reduced with increasing number of substituents bonded to *s*-triazine ring. One should point that the polyester resins modified with compounds containing *N*-phenyl-*N*-

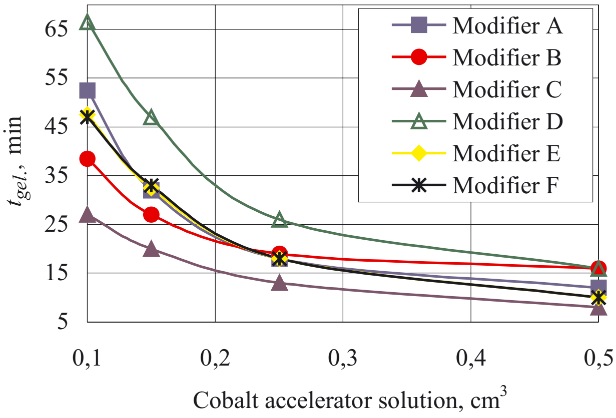


Fig. 3. Effects of kind of modifier and amount of cobalt accelerator solution on gelation time ($t_{gel.}$) of UP resins; conditions of gelation: 0.25 wt. % of modifier and 0.5 g of initiator/25 g of resin (standard)

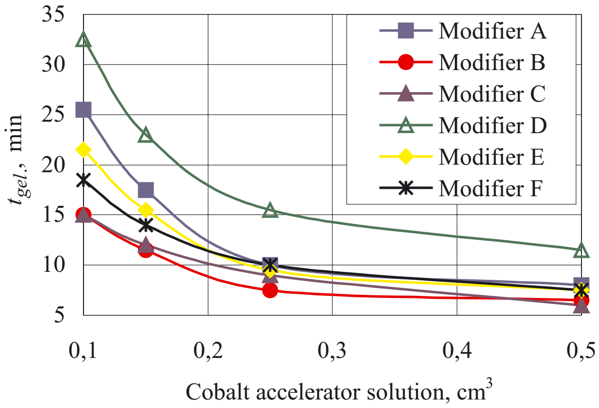


Fig. 4. Effects of kind of modifier and amount of cobalt accelerator solution on gelation time ($t_{gel.}$) of UP resins; conditions of gelation: 0.25 wt. % of modifier and 1.0 g of initiator/25 g of resin (over standard)

-(2-hydroxylethyl) substituents exhibit shorter gelation times than those where *s*-triazine rings are substituted with *N,N*-bis(2-hydroxylethyl) groups.

Thermal properties

T a b l e 1. Thermal characteristics of modified and cured UP resins

Modifier		Temperature of decomposition, °C				
kind	amount built into UP wt. %	beginning	5 %	20 %	50 %	at end
No modifier	—	60	230	300	340	650
A	1.75	100	250	330	390	700
B	2.00	60	220	300	330	630
C	1.75	50	185	305	345	655
D	1.25	40	260	330	350	650
E	1.25	50	260	240	380	710
F	1.00	60	200	300	330	635

Table 1 consists the results of DTA investigations of UP resins containing A—F modifiers. The average temperature of decomposition beginning was *ca.* 60 °C, but the clear weight loss was not observed before *ca.* 350 °C, where the endothermic peak appeared. The data collected in Table 1 indicate that the cured resins modified with 1.75 wt. % of modifier A showed the highest thermal stability. In the case of resins modified with 1.75 wt. % of modifier C or 1.0 wt. % of modifier F no significant improved of thermal stability was observed.

Stability

In general one can state that the stability of modified resins containing *N*-phenyl-*N*-(2-hydroxyethyl) or *N,N*-bis(2-hydroxyethyl) groups becomes worse and worse as the number of substituents at *s*-triazine ring increases (Fig. 5).

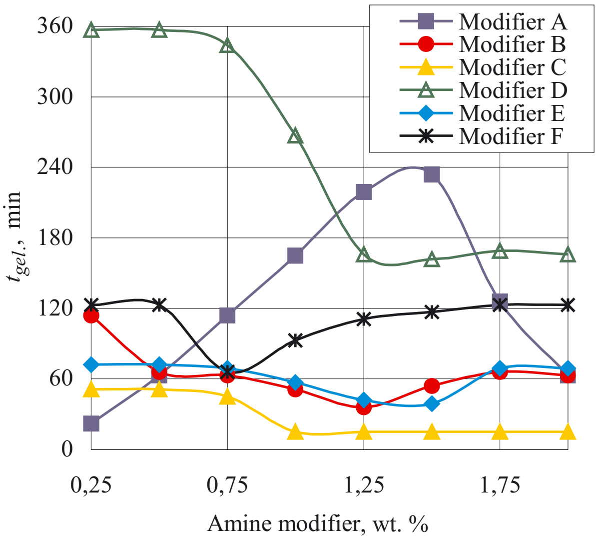


Fig. 5. Effects of kind and amount of amine modifier on stability at 70 °C of UP resins

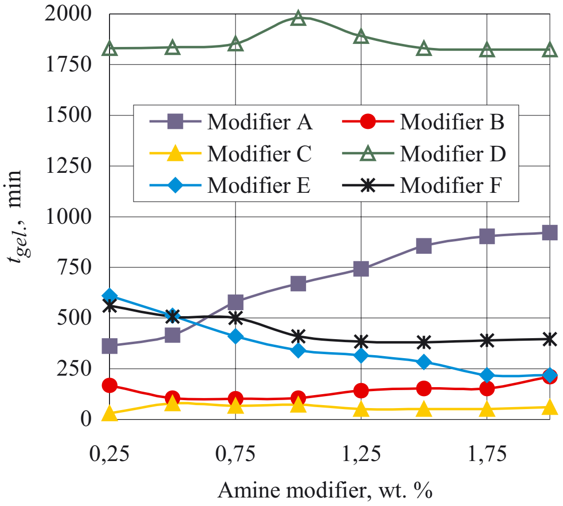


Fig. 6. Effects of kind and amount of amine modifier on stability at 70 °C of UP resins containing 0.3 wt. % of benzyltriethylammonium chloride

Unsaturated polyester resin without any modifier show standard stability of 824 h. To improve this property of modified resins 0.3 wt. % of benzyltriethylammonium chloride were used [22]. The ammonium salt improved the stability of all resins. It was observed that the resins modified with the compound containing just one substituent at *s*-triazine ring (modifiers A and D) show much higher stability than other modified resins (Fig. 6). This can be explained the following way. The modifiers with one or two hydroxyl groups are built into the linear part of a polymer. The other modifiers produce branches. This might be the reason of reduced stability of some modified resins and also of their higher reactivity.

CONCLUSIONS

— In order to reduce gelation time the resins should be modified with 1.25 wt. % of amine modifiers. The initiator should be butanone peroxide (50 wt. % solution of the initiator in dibutyl phthalate) and cobalt(II) octanoate accelerator (1 wt. % solution in styrene).

— The admixture of cobalt accelerator used in the amount 0.1 to 0.3 cm^3 per 25 g of resin considerably reduces gelation time both in case of the standard (0.5 g) or over-standard (1.0 or 1.5 g) amount of initiator.

— The optimal curing system for all the resins modified with amine modifiers is to use 0.5 g of peroxy initiator and 0.25 cm^3 of cobalt accelerator per 25 g of resin.

— By building into the resin structure any of the modifiers prepared in this work (A—F) one can significantly reduce gelation time as compared with unmodified resin. Since the resulting gelation time ranged from 3.5 to 88.0 min, one can tailor the resin to show gelation time suitable for a given application.

— Introduction of any of the modifiers into the structure of unsaturated polyester resin considerably reduced the storage time as compared with that of unmodified resin. Addition of 0.3 wt. % of ammonium salt evidently improves the storage stability of all modified resins.

— The highest thermal stability was observed for the resin containing in this structure modifier A: 2-[*N*-phenyl-(2-hydroxyethyl)amine]-4,6-dimethoxy-1,3,5-triazine. Its temperature of the beginning and the end of thermal decomposition were on the average by 40 °C higher than those of the resin without a modifier.

REFERENCES

1. Kłosowska-Wołkowicz Z., Królikowski W., Penczek P.: "Żywice i laminaty", WNT, Warszawa 1986.
2. Kłosowska-Wołkowicz Z., Jedliński Z.: *Polimery* 1970, **15**, 1.
3. *DD Pat.* 227 711 (1986); *CA* 1986, **104**, 208 379d.
4. *Jap. Pat.* 2 250 025 (1987); see www.derwent.com
5. *Jap. Pat.* 1 026 653 (1989); see www.derwent.com
6. *Ukrainian Pat.* 1 467 137 (1990); see www.derwent.com
7. *DE Pat.* 3 345 102 (1985); *CA* 1985, **103**, 196 858y.
8. Attia I. A., Abdel-Halim M. S., Abdel-Azim A. A.: *Polym. Bull.* 1995, **34**, 377.
9. Penczek P., Kłosowska-Wołkowicz Z.: *Polimery* 1997, **42**, 292.
10. *DE Pat.* 3 643 788 (1988); *CA* 1989, **110**, 39 557b.
11. *USA Pat.* 4 775 597 (1988); *CA* 1989, **110**, 40 630b.
12. *Europ. Pat.* 271 385 (1988); *CA* 1989, **110**, 98 628y.
13. Duliban J.: *Macromol. Mater. Eng.* 2001, **286**, 624.
14. Jada S. S.: *Makromol. Chem.* 1982, **183**, 1763.
15. Horner L., Schloenk E.: *Angew. Chem.* 1949, **61**, 711.
16. Kłosowska-Wołkowicz Z., Penczek P., Gąsior R.: *Plaste Kautsch.* 1976, **23**, 251.
17. Porejko S., Fejgin J., Zakrzewski L.: "Chemia związków wielkocząsteczkowych", WNT, Warszawa 1972.
18. Jada S. S.: *Ind. Eng. Chem. Prod. Res. Dev.* 1983, **22**, 14.
19. Kharash M. M., Pauson P., Nudenberg W. J.: *J. Org. Chem.* 1953, **38**, 322.
20. Duliban J.: *Macromol. Mater. Eng.* (to be published).
21. Duliban J.: *Macromol. Mater. Eng.* (to be published).
22. Oleksy M., Galina H.: *Polimery* 2000, **45**, 541.