

## Activity of a modified redox system for polymerization of unsaturated polyester resins

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**Summary:** A modified redox system intended for initiation of radical polymerization of unsaturated polyester resins was investigated. The main feature of this modification was the presence of an additional accelerator – sodium formaldehyde sulfoxylate (also known as ‘Rongalit’). Rongalit acts as a reducer in hydrophilic medium. The interaction between Rongalit and the hydrophobic ingredients of the reactive mixture occur at the boundary surfaces between the different phases.

The specific influence of the initiating system’s components over the polymerization kinetics was estimated. The technological time needed for gelling and then - for complete hardening of the resin was determined. The end properties of the cured polyesters as well as those of their derivative glass-fibres-reinforced composites were not found to be dependent on the mode of initiation of the polymerization process.

**Keywords:** orthophthalic unsaturated polyester resins; glass-fibres-reinforced polyesters; sodium formaldehydesulphoxilate (Rongalit); dimethylaniline

### Introduction

The unsaturated polyester resins cure as a result of radical co-polymerization involving oligoesters and molecules of their vinyl solvent like styrene. They form specific cross-linked thermoset network. This process is initiated by redox system, containing a catalyst - organic peroxide, and accelerators (promoters) as reducing agents. The commonly used accelerators are some quaternary ammonium halides as well as some organic aliphatic or cycloaliphatic salts - soaps of transitional metals like cobalt octoate or cobalt naphthenate [1,2,3]. There are experiments reported on the possibilities of speeding up the radical polymerization at its earliest stage by making use of a modified initiating system that contains sodium formaldehydesulphoxilate as co-accelerator [4,5,6]. The presence of Rongalit reduces the duration of the co-polymerization induction period. The modified redox system is efficient enough even in harsh environments like low temperature, extremely high presence of moisture or inhibitors overdose.

The reported modification uncovers also an attractive new opportunity to reduce the content of DMA (dimethyl aniline) at the expense of Rongalit (leastwise when this is ecologically reasonable with a view to the high toxicity of DMA concomitant its

undoubted efficiency). To this end there was investigated the dependence between the activity of the modified redox system and its composition.

## Experimental

*Materials:* Unsaturated polyester resin (UPER) - orthophthalic type: 'Vinalkyd 550 PE', a product of 'Orgachim' (Bulgaria); Cobalt octoate ( $\text{CoOt}_2$ ) - 'Accelerator NL - 49 P', a product of 'AKZO'; Dimethylaniline (DMA) - 'Accelerator NL 63-10 P', a product of 'AKZO'; Sodium formaldehyde sulfoxylate:  $\text{HOCH}_2\text{SO}_2\text{Na}\cdot 2\text{H}_2\text{O}$  - Rongalit<sup>®</sup> (or 'Ro' - as it was marked in some figures and tables); Cyclohexanone peroxide (CHPO) 'Cyclonox LT-50', a product of 'AKZO'; Methyl ethyl ketone peroxide (MEKP); Benzoyl peroxide (BP); Cumene hydroperoxide (CUHP); Tertiary butyl perbenzoate (TBPB); Chopped 'E' glass-fibres mat, trademark of 'Ahlström' (Finland) - 'M 5057 122645', with surface density of  $450 \text{ g/m}^2$ .

*Methods:* Resin hardening was tested using small quantities of resin - 50 g. Such doses are sufficient for achieving the necessary heat effect (big enough to compensate all heat losses during the polymerization). The ingredients of the initiating system were added into the resin by vigorous stirring successively, as follows:  $\text{CoOt}_2$ , DMA, Rongalit, peroxide.

The viscosity of the polymerizing resin was measured using apparatus 'Rheotest'. The gel time was established using automatic gel timer.

The achieved degree of resin hardening was estimated in terms of the Barcol test using Barcol hard-meter 934; the required initial hardness was more than 20 units.

Glass-fibres-reinforced laminates  $200 \text{ mm} \times 200 \text{ mm}$  with standard thickness of 4 mm were made using 'cold press-moulding' technology. The total content of glass-fibres reinforcement was at about 31–32 mass%. The moulding conditions were, as follows: initial temperature of  $25^\circ\text{C}$ , constant pressure of 0,25 MPa, operation time - 20 min to 40 min (depending on the activity of the redox system). The cured laminates were annealed at a constant temperature of  $80^\circ\text{C}$  during 24 hours. The samples for standard mechanical tests were cut using diamond disc. The **tensile strength** and the **bending strength** were determined using dynamometer 'TT DM INSTRON' according to standards ISO 527 and ISO 178, respectively (at constant speed of deformation 50 mm/min). The **impact strength** was measured according to standard ISO 179 using appliance 'CEAST 6545/000'.

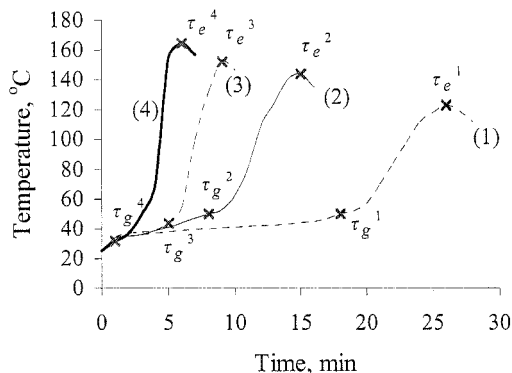
## Discussion

Series of tests were carried out to determine the influence of different amounts of Rongalit, DMA, as well as their combinations in certain ratios, added to the initiating system CHPO/ $\text{CoOt}_2$ , over the polymerization kinetics. They resulted in revealing of a useful new opportunity to intensify the cure of orthophthalic polyester resins.

Figure 1 illustrates the correlation between the reaction heat-output (without any external heating) and the degree of conversion of the oligoesters and styrene molecules into a cured polymer material. The exothermal curves describe the reaction kinetics.

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<sup>®</sup> 'Rongalit' ( $\text{CH}_3\text{NaO}_3\text{S}\cdot 2\text{H}_2\text{O}$ ) is registered trademark of BASF.



**Figure 1.** Composition of the redox system vs. the rate of co-polymerization of orthophthalic UPER, where: **curve 1)** 'Standard': 1.0 % CoOt<sub>2</sub> + 1.0 % CHPO (mass% regarding to UPER); **2)** 1.0 % CoOt<sub>2</sub> + 0.1 % DMA + 1.0 % CHPO; **3)** 1 % CoOt<sub>2</sub> + 0.1 % Rongalit + 1.0 % CHPO; **4)** 1.0 % CoOt<sub>2</sub> + 0.1 % DMA + 0.1 % Rongalit + 1.0 % CHPO

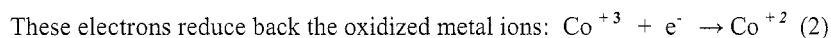
All the curves are notable for their specific 'S'-shape character. As a whole, their course can be divided into three main sections: (i) An almost linear initial sector reflects the slow increase of the temperature in the induction period of the polymerization; (ii) The reaction heat output rapidly increases as the spontaneous chain reaction of fast growth of the polymer macromolecules and forming of spatial thermoset network get started. This effect is well described by the exponential section of the kinetic curves. It makes for further decomposition of the peroxides - a precondition for arising of numerous new polymer chains. Thus, the inclusion of great many new monomer units into the already formed polymer structures is brought forward. Obviously, an auto-catalyzing process starts developing. The molecular weight increases significantly in a relatively short time. The orthophthalic UPER macromolecules grow highly branched and cross-linked. The viscosity of reactive mixture increases adequately. The resin quickly gels and warms up. The phenomenon gel effect appears. The resin temperature quickly reached the maximum, known as exothermal peak; (iii) passing this extremum, the temperature starts decreasing as from now on the process of polymerization slows down.

Curve 1 (fig.1) shows the typical course of the process of orthophthalic UPER polymerization. The gel time ( $\tau_g^1$ ) was at about 19–20 min. The exothermal peak was reached after 25–26 min ( $\tau_e^1$ ).

The gel time was diminished more than twice by adding DMA as an additional promoter (curve 2). Thus, the exothermal peak appeared after 14–15 min ( $\tau_e^2$ ).

The presence of Rongalit as co-accelerator in the redox system intensified even more the polymerization reaction (curve 3). The resin gelled after 5–6 min ( $\tau_g^3$ ) and the exothermic peak was registered after 10–11 min ( $\tau_e^3$ ).

The mechanism of DMA accelerating action is well studied but the distinct promoting effects of various Rongalit amounts are still obscure to a certain extent. According to some publications [7,8] the Rongalit oxidation is accompanied with electron emission:



This cycling process of fast alternating changes of the metal oxidation states keeps up the promoter's activity.

Both the metal ions and Rongalit molecules are in the polar phase. On the other hand, the catalyst decomposition takes place in the colloid micelles. Their surfaces are the only area where the hydrophilic complex of reduced metal ions and the hydrophobic phase of vinyl monomers and organic peroxides can react with each other.

The hydroperoxides act as bi-functional compounds due to the combination of polar groups and hydrophobic organic segment in the same molecule. Their radicals are typical organic compounds that can easily migrate into the volume of organic phase. The reaction equilibrium is shifted to direction of radicalizing the oligoesters and styrene molecules and their subsequent radical co-polymerization. In most of the tests Rongalit was added to UPER dissolved in a polar solvent – i.e. its low concentrated water solutions or diluted mixtures of glycols and polyglycols. This practice handicapped its complete interaction with the other components of the initiating system into the hydrophobic resin medium. Intensive stirring of the reactive mixture particularly solved the problem.

$\text{CoOt}_2$  as soap is supposed to contribute for obtaining a fine emulsion with enlarged inter-phase boundary surface where the co-accelerators molecules are concentrated. The Rongalit, in turn, contains an organic group. This facilitates its contact with the components of the hydrophobic phase.

The suggested mechanism of initiation was somewhat confirmed also by the miscarriage of all attempts to substitute Rongalit for  $\text{Na}_2\text{SO}_3$  as an alternative co-accelerator in the redox system.

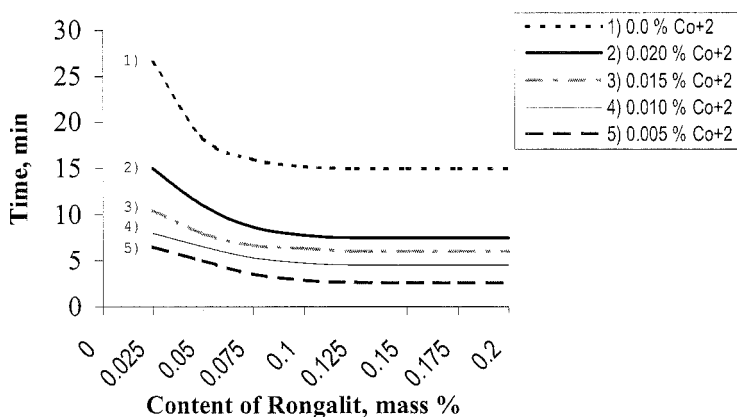
The Rongalit solutions into mixtures of water-diluted glycols and polyglycols were even more efficient. Some of them and especially these containing polyglycols with molecular weight more than 400 added to UPER formed emulsions 'in situ'.

The activating effect of Rongalit as co-accelerator is due to the blocking of the inhibitors as well. Manufacturers usually add small amounts (at about 80+200 ppm) of inhibitors like hydroquinone as stabilizers. They prevent the resins from homolytic polymerization during their storage and transportation. In aggressive oxidizing environments the hydroquinone transforms into semi-quinone radical or quinone. These compounds can be recombined with peroxide radicals or with polyester macroradicals. The result is premature termination of the growing polymerization chains (other words, the hydroquinone and its derivatives act as 'radicals traps'). In the presence of Rongalit such negative trends are strongly restricted that explains the elimination of the inhibiting action of even considerable doses of hydroquinone added to UPER mixtures containing Rongalit (Ro) (table 1).

**Table 1:** Influence of the redox system composition and the content of hydroquinone on the gel and cure time of the orthophthalic polyester resin. Notes: 1. N – ‘Normal’ content ( $80 \pm 100$  ppm) of hydroquinone added into resin by the producer to guarantee its stability; 2. ‘N + ...’ - Additional hydroquinone amount; 3.  $\text{CoO}t_2 - \text{CoO}t_2$  is used as a 6 % solution (1 %  $\text{Co}^{+2}$ ).

Hydroquinone content, ppm	Composition of the initiating system				Gel time, min	Cure time, min
	CHPO, %	* $\text{CoO}t_2$ , %	DMA, %	Ro, %		
N	1.0	1.0	-	-	19	30
N	1.0	1.0	0.10	-	8	16
N + 500	1.0	1.0	0.15	-	-	-
N + 500	3.0	1.8	0.35	-	-	-
N + 500	1.0	1.0	-	0.05	3	12
N + 500	1.0	1.0	0.10	0.05	2 - 3	12
N + 500	2.0	0.8	0.15	0.10	1 - 2	9
N + 2500	2.0	0.8	0.15	0.10	2 - 3	13

The proportions between the components of the redox system also have an essential influence upon the resin’s gel and cure time. For that reason series of experiments were held with varying concentrations of the different co-accelerators.



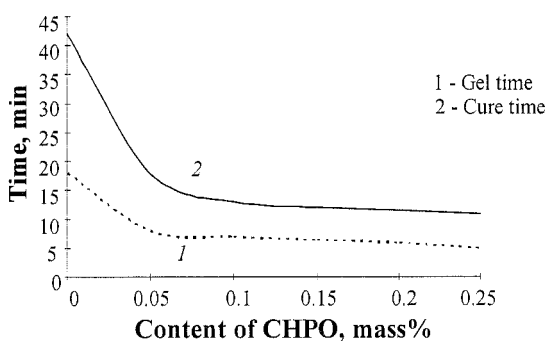
**Figure 2.** Gel time ( $\tau$ ) of UPER containing 1 wt% CHPO vs. the content of Rongalit and  $\text{CoO}t_2$

The results revealed a useful new opportunity for forcing the resin gelling by modification with small doses of Rongalit even in absence of any other co-accelerators at all (fig.2, curve1). In this particular case UPER almost lost ability to cure and retained its gel consistence very long - even for days. This phenomenon implies some more complicated mechanism of the initiation of the resin copolymerization in the presence of Rongalit than the described above. However, it needs many additional experiments in order to be accurately explained.

Curve 1 (fig.2) shows also an increasing activity of the initiating system in the case of reduced content of  $\text{CoO}t_2$ . A threshold concentration of  $0.00003 \text{ mass}\% \text{Co}^{+2}$  ions was detected. Below this limiting content of  $\text{CoO}t_2$  the resin gelled but did not hardened. When the  $\text{Co}^{+2}$  concentrations were lower than  $0.0006 \text{ mass}\%$  the resin gelled and cured rapidly but the samples remained gluey for several days. The Barcol hardness was relatively low.

**Table 2:** Gel-time, cure-time and degree of cross-linking vs. the content of  $\text{Co}^{+2}$  (Note: The concentration of CHPO in the resin was 1.0 wt%; the concentration of Rongalit was 0.1wt%)

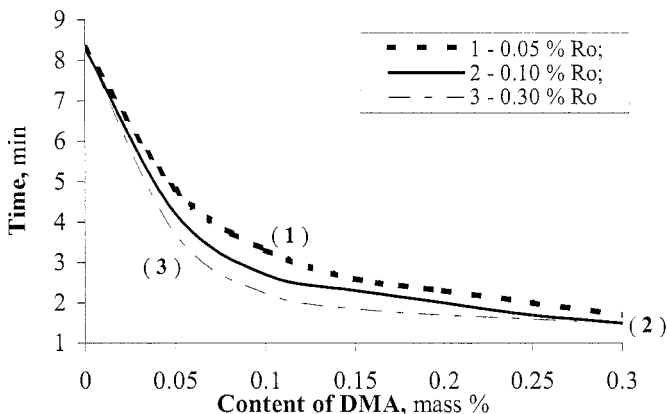
Concentration of $\text{Co}^{+2}$ ions, mass %	Gel time, min, s	Cure time, min	Barcol hardness		Surface appearance
			72 hours	60 min	
0	18' 15''	-	-	-	Gluey
$4 \cdot 10^{-5}$	3' 45''	27	6	16	Gluey
$6 \cdot 10^{-5}$	4' 30''	22	10	18	Rigid
$8 \cdot 10^{-5}$	6' 15''	14	16	26	Rigid
$1 \cdot 10^{-4}$	7' 30''	17	19	32	Rigid
$1,8 \cdot 10^{-4}$	8' 00''	20	20	31	Gluey



**Figure 3.** Gel time (curve 1) and cure time (curve 2) of the resin vs. the concentration of CHPO in the modified redox system

The graphs (fig.3) show that CHPO concentration higher than 1.0 mass% accelerate moderately both the gelling and hardening processes. Obviously, by varying the concentrations of the different accelerators as well as by changing their mutual proportions we can regulate more precisely the speed of resin thickening.

Figure 4 confirms the expected high efficiency of DMA. When DMA was combined simultaneously with the two other accelerators -  $\text{CoOt}_2$  and Rongalit, a synergic effect appeared: the reaction speed exceeded significantly these of the combinations DMA/ $\text{CoOt}_2$  and DMA/Rongalit. It seems worthwhile to investigate how exactly the content of the tertiary amine influences the polymerization process.



**Figure 4.** DMA content vs. the gel-time ( $\tau$ )

The initiating system contains 1wt% CHPO, 1 wt% CoOt<sub>2</sub> and different amounts of Rongalit.

Figure 4<sup>th</sup> shows that when the amount of DMA is big enough, the Rongalit concentration has not considerable influence on the gel-time.

The results reveal an attractive new opportunity for a drastic shortening of the gel-time by making use of some more complicated but appropriate combinations of different co-accelerators including Rongalit.

It is known that the activity of initiating systems depends on the type of peroxides used. We have investigated here the efficiency of the modified redox system in the case of using several different peroxides (table 3).

**Table 3:** Gel-time vs. the type of peroxide in the composition of modified redox system containing constant amounts of ingredients, as follows: 1% peroxide, 1% CoOt<sub>2</sub> and 0.1% Ro.

Peroxides:	Gel time [min, s]
Methyl Ethyl Ketone Peroxide (MEKP)	1' 35''
Cyclohexanone Peroxide (CHPO)	2' 25''
Benzoyl Peroxide (BP)	2' 25''
Cumene Hydroperoxide (CUHP)	4' 50''
Tertiary Butyl Perbenzoate (TBPB)	4' 30''

MEKP appeared as the most efficient but the results, obtained at standard room temperature (18 - 25°C) with CUHP and TBPB, were also good enough (although TBPB is designed for high-temperature polymerization).

Table 4 presents the mechanical properties of the tested polyesters and glass-fibres-reinforced plastics with polyester matrix. The samples are obtained by making use of the modified initiating system varying the concentrations of the co-accelerators and their mutual proportions.

**Table 4:** Mechanical properties of cured polyesters and reinforced polyester laminates with 32-35 mass% fibreglass mat content, that are manufactured using 1mass% CHPO and different quantities of Rongalit and \*CoOt<sub>2</sub>

SAMPLES	ACCELERATORS		MECHANICAL PROPERTIES			
	CoOt <sub>2</sub> , wt %	Ro, wt %	Tensile Strength, MPa	Tensile Module, MPa	Bending Strength, MPa	Impact Strength, J/m <sup>2</sup>
POLYESTERS	1.0	0.0	31	3200	82	5.0
	0.6	0.1	29	3100	84	3.5
	1.0	0.1	30	3000	84	5.0
	1.8	0.1	32	3250	83	4.5
Glass-fibres reinforced composites	1.0	0.0	74	7200	140	6.6
	0.6	0.1	72	7050	142	6.4
	1.0	0.1	73	7170	144	6.8
	1.8	0.1	75	7150	138	6.5

## Conclusion

The modified initiating redox system intended for UPER co-polymerization has been elaborated. This redox system involves sodium formaldehydesulphoxilate (Rongalit) as a co-accelerator, together with the traditional promoters. Rongalit contributes for speeding up the polymerization process. Thus, in certain occasions the gel time can be shortened just to few minutes. Another advantage is the opportunity to compensate at least partly the toxic DMA at the expense of Rongalit as efficient co-accelerator.

The addition of Rongalit also eliminates the inhibiting effect of even extremely high doses of hydroquinone.

It is established that the activity of the modified redox system decreases as the concentration of Cobalt octoate in the reactive mixture increases.

There is suggested a mechanism of interaction of the components of the initiating system with each other that occurs at the inter-phases surface.

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