

Effect of Silicate Modifier on the Emission of Harmful Compounds from Phenolic Resin used in Cold-Box Technology

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Abstract

In many foundries, the requirements placed on castings production have risen mainly over the few years. Further trends in recent years have been the ever increasing level of automation and introduction of new alloys, especially composites. On the other hand, the foundry environment has become increasingly difficult because is used many organic binders. Environmental regulations will be further tightened up. These processes are pursued at national, European and global level. Conformity with emission limits is becoming increasingly difficult. The problem is emission of aromatic hydrocarbons, phenol, odours and other harmful compounds to environment. The main purpose of many companies is reduction of this toxins. The new cold-box systems (based on phenolic resins) try to reduce the emission by introducing into the resin structure silicate modifiers. Research presented of this article evaluate the effectiveness of these methods. The results show comparison of two resins ("without" and "with" silicate modifier) for assessment of emission of harmful aromatic hydrocarbons and phenol.

Keywords: Environment protection, Resin, Aromatic hydrocarbons, Phenol, Emission, Cold-Box

1. Introduction

The cold box system was originally understood to be the phenolic/urethane/amine process, but now describes any core binder process that uses a gas or vaporized catalyst to cure resin coated sand while it is in contact with a room temperature pattern. The polyurethane cold-box process is based on the reaction of two components (Fig. 1):

- Part 1: a polyaddition of the phenol-formaldehyde resin;
- Part 2: the isocyanate, is initiated through basic catalysis, usually by means of gassing with a tertiary amine [1].

The cold box processes have eliminated the need for expensive, inconvenient heat curing. They offer advantages of dimensional accuracy, productivity and potentially higher quality than other

core and mould systems. With the exception of the silicate/CO₂ process, all the cold box systems have the typical blow, gas, purging, strip core making sequence [2].

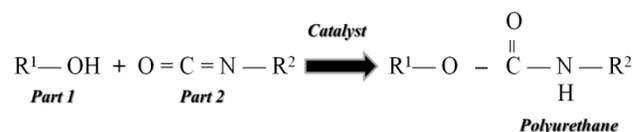


Fig. 1. Reaction of cold-box process

The cure cycle is relatively fast and can be completed within seconds. The most popular systems, which are all in this category are presented on Figure 2 [3].

4 and 5. Curves were recorded in the temperature range of 20-1000°C, in the air atmosphere.

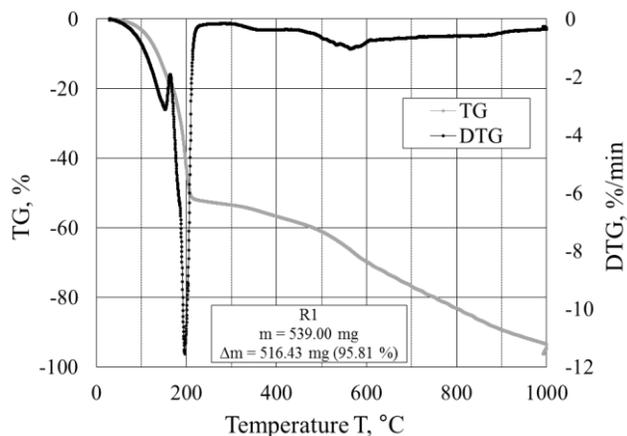


Fig. 4. Thermogram TG/DTG of resin R1

The process of R1 can be subdivided into three stages based on the DTG profile. The first stage shows a mass loss of 19.66 % for drying the sample between 25 and 170°C (small endothermic effect); surface moisture and inherent moisture are emitted in this stage [12, 13]. The second stage is fast thermal decomposition between 180 and 450°C; the maximum mass loss (about 41.12 wt.% of the total weight) occurs in this stage. The third stage shows 32.65 wt.% of the total mass loss due to further decomposition of resin R1. This last stage has a wide temperature range, from 500°C to the end of this experiment (1000°C) – second small endothermic effect. During the process, there are three peaks of the DTG curve (mass loss rate) at 152.92, 195.95 and 562.52°C in first, second and last stage degradation, respectively. The maximum mass loss rate of 11.5 %/min occurred at 195.94°C.

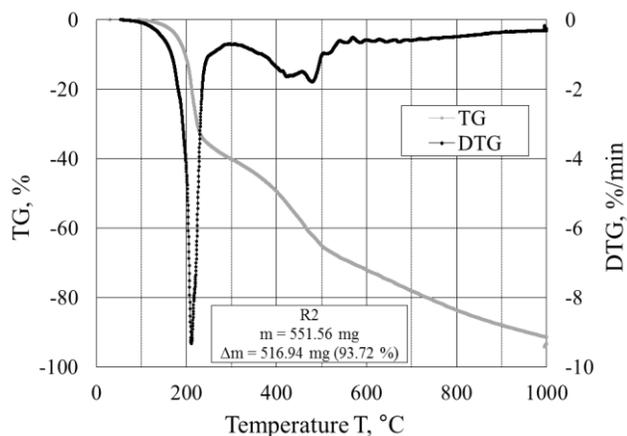


Fig. 5. Thermogram TG/DTG of resin R2

The thermogram of R2 is little different. The first stage shows a maximum of mass loss of 39.93% for drying the sample between 25 and 250°C (fast thermal decomposition). The second and third stage are small endothermic effects: I – from 350 to

450°C (14.17 wt.% of the total weight) and II – from 460 to 500°C (6.59 wt.% of the total weight). There are three peaks of the DTG curve (mass loss rate) one in the first and two in the second stage. The maximum mass loss rate occurred at 210.45°C (9.33 %/min).

The IR spectra for resins R1 (a) and R2 (b) are given in Figs. 6 and 7.

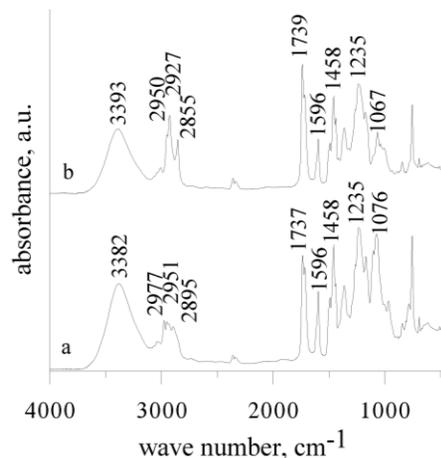


Fig. 6. IR spectra of the resins R1 (a) and R2 (b) in the range of wave number 4000-1100 cm^{-1}

The bands at the wave number 3393 and 3382 cm^{-1} corresponds to the O-H stretching vibrations (Fig. 6). In the range of 3000-2850 cm^{-1} the vibrations attributed to C-H bonds (both CH_2 and CH_3) are recorded. Appearance of the bands in the range of wave number between 1750-1700 cm^{-1} indicates the occurrence of vibrations of C=O bonds [14].

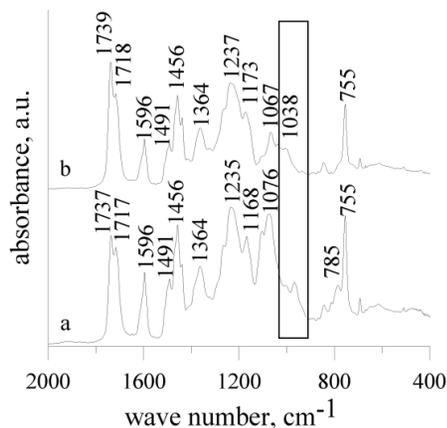


Fig. 7. IR spectra of the resins R1 (a) and R2 (b) in the range of wave number 2000-400 cm^{-1}

The bands at the wave number 1596 and 1491 cm^{-1} are associated with C=C bonding in the aromatic ring. Appearance of the band at the wave number 1364 cm^{-1} is attributed to O-H phenol vibrations in the plane [15, 16]. Band at the wave number 1235 cm^{-1} is assigned as asymmetric C-C-O stretching bonds, while at 1168 cm^{-1} as deformation vibrations of C-H bond in the plane [17]. Within the range of 1080-1016 cm^{-1} there are bands that can be

attributed to single C-O bonds associated with the -C-OH stretching groups [18]. At the wave number 755 cm^{-1} recorded the band of vibrations beyond the plane of C-H bond (Fig. 7).

The chemical structure of both samples of phenolic resins observed on FTIR spectra in the range of wave number $4000\text{--}1100\text{ cm}^{-1}$ is very similar. Appearance differences in the modified resin (R2) are observed in the range of wave number $1080\text{--}1000\text{ cm}^{-1}$. A band at wave number 1038 cm^{-1} appears, which indicates the addition of a silicate modifier (Fig. 7, spectrum b). This band is characteristic of Si-O stretching vibrations [19-23].

The chromatograms for resins R1 and R2 are given in Figs. 8 and 9. The temperature range was coherent to obtained data from TG/DTG curves. The pyrolysis gas chromatography (Py-GC/MS) method is based on transforming a solid sample (about 5 mg) into gas by heating in an atmosphere of inert gas (e.g. helium) in a pyrolyzer, which is accompanied by thermal decomposition [24]. The temperature range of work of pyrolyzer is $240\text{--}1300^\circ\text{C}$. The obtained mixture of compounds is separated on a chromatographic column in a chromatograph coupled with mass spectrometer. A temperature program was applied: an initial temperature of 40°C was held for 3 min; ramped $3^\circ\text{C}/\text{min}$ up to 100°C and held for 3 min, and then 250°C with a heating rate of $20^\circ\text{C}/\text{min}$ was maintained for 3 min (helium carrier gas at $1\text{ ml}/\text{min}$, sample split ratio 1:30) [25]. Conditions of mass spectrometer: the full range mass number/charge number (m/z); electron ionisation (70 eV) at a temperature of 250°C [26].

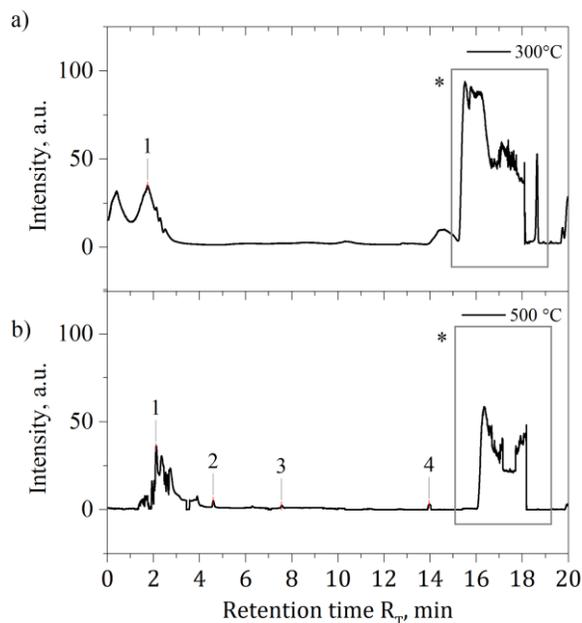


Fig. 8. Chromatogram for resin R1

Attention was focused to the emission of aromatic hydrocarbons and phenol. The list of obtained compounds was shown in Tables 2.

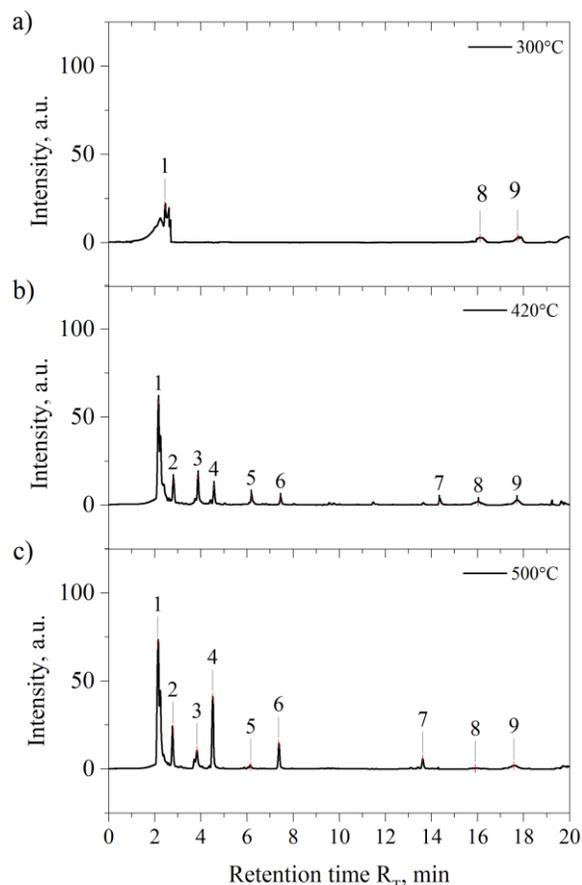


Fig. 9. Chromatogram for resin R2

Table 2. Results of the qualitative analysis of Py-GC/MS research

	No.	Compound	Retention time R_T , min		
			300°C	500°C	
R1	1	Carbon dioxide	2.01	2.12	
	2	Benzene	n.a.	4.53	
	3	Toluene	n.a.	7.67	
	4	Styrene	n.a.	14.05	
	*	thermal degradation products of plant solvents and phenol	15-19.00	16-18.00	
	No.	Compound	Retention time R_T , min		
			300°C	420°C	500°C
R2	1	Carbon dioxide	2.03	2.09	2.05
	2	Cyclopentadiene	n.a.	2.76	2.79
	3	Formamide	n.a.	3.92	3.96
	4	Benzene	n.a.	4.55	4.56
	5	Glycolic acid	n.a.	6.12	6.18
	6	Toluene	n.a.	7.65	7.69
	7	Styrene	n.a.	13.98	13.93
	8	Phenol	16.32	16.36	16.39
	9	m-Cresol	17.89	17.95	17.94

At 300°C carbon dioxide, thermal degradation products of plant solvents (resin R1) and phenol (both resins) were found. For resin R2 the temperatures 420°C and 500°C gave the similar products of thermal degradation. At 500°C some marks of benzene, toluene and styrene decomposition were found in the products of both resins.

For the resin R1 the chromatograms have much more signals than for resin R2. The characteristic area for resin R1 within a retention time (R_T) range of about 15-19 min includes a number of signals that derived from the decomposition of plant solvents and phenol. As the temperature of decomposition increases, these compounds will be more pronounced in the chromatograms.

Chromatogram for the resin R2 has much less signals than for R1. In the products of thermal degradation were identified some hydrocarbons (benzene, toluene and styrene), phenol and its derivatives (e.g. m-cresol). At temperature 420°C and 500°C also were founded cyclopentadiene (reagents in organic synthesis), formamide (solvent for resins and plasticizers), glycolic acid (useful intermediate for organic synthesis, in a range of reactions including e.g. esterification or long chain polymerization).

5. Conclusions

Based on the obtained results, the following conclusions can be drawn:

- the thermal analysis of tested resins R1 and R2 allows the indicate of characteristic temperature points accompanied by a loss of weight. The first one was probably related to the loss of solvent (main component of resin), the next one to the decomposition of C-H bonds and phenol;
- the FTIR studies confirm occurrence of silicate modifier in resin R2;
- the Py-GC/MS analysis showed that silicate modifier reduces emission of some hydrocarbons and products of phenol (planning quantitative analysis will be confirm the difference between tested resins - mainly decrease amount of emission of benzene);
- the addition of silicate modifier also affects the reduction on plant solvents, so resin R2 in more friendly for environment;

Because of the limits of the Py-GC/MS apparatus (fused silica column), it is impossible to delineate the silicate products in the tested samples (mainly resin R2).

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