# Polymer composites with ferrocene derivatives for fire-safe construction

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ABSTRACT: Wide use of polymers in the modern construction industry requires careful examination and optimization of operational properties related to fire safety. As an agent for smoke suppression, fireretardant ferrocene was employed decades ago. In spite of this, to date, there are limited data related to the influence of ferrocene and its derivatives on the properties of several polymer composites important for construction. The aim of the present work is to investigate the suitability and effectiveness of ferrocene and different ferrocene derivatives as admixtures for two types of polymer composites. We discussed the experimental results of several laboratory tests. It is shown that ferrocene derivatives of relatively low volatility can be successfully used as efficient smoke suppressors and fire retardants. This is due to the barrier layer formation on the surface of the burning material. Such layer prevents the penetration of pyrolysis products and slows down the spread of the flame. At the same time, the results indicate that probably no universal chemical agent allows to achieve the preferred values of all operational properties related to fire safety at once: optimal values for weight loss, rate of decomposition, limiting oxygen index and smoke formation factor cannot be simultaneously reached in any single point of factor space.

## 1 INTRODUCTION AND PRIOR WORK

One objective of fire-safe construction involves the development of effective admixtures for flammable building materials, in particular, for polymer composites. Fire resistance of carbonizing polymers greatly depends on their chemical structure and the amount of synergists and smoke suppressors. It is known that ferrocene is an efficient smoke suppressor (Kulev et al. 1986, Ushkov et al. 1988). Its addition leads to a decrease in smoke density caused by sooting during the combustion of unsaturated (Zhang 1994) and saturated (Kasper 1999) hydrocarbons. Ferrocene structures in polymer chains lead to thermal stability and fire resistance (Kishore 1991); though at least for several ferrocene derivatives, there is a negative correlation between smoke suppression and flame retardancy (Carty 1996). As a methane flame inhibitor, ferrocene is as efficient as iron pentacarbonyl (Linteris 1991). The high efficiency of ferrocene is due to the fact that during oxidation. it acts as a source of iron-containing intermediates with high specific surface and catalytic activity. Ferrocene acts as a catalyst of the heterogeneous carbon oxidation process, promotes almost smokefree burning of organic polymers and increases the completeness of combustion (Reshetova 1975).

Some aspects of the combustion catalysis of flammable materials by ferrocene have been examined in the literature (Sinditsky et al. 2014). Ferrocene influences the pyrolysis of polymers, inhibits oxidation and shows high reactivity to gaseous HCl, forming iron chloride during the reaction (Kulev et al. 1986).

Considering building materials for fire-safe construction, the drawback of pure ferrocene is due to its relatively high volatility at temperatures above 150 °C, despite the fact that ferrocene demonstrates thermal stability up to the temperature of 470 °C (Fomin 2007, Zhukov 2000). Ferrocene decomposes with a high rate only at temperatures higher than 550 °C (Fomin 2007). Because of this, there is a need to identify its derivative compounds that have similar fire and smoke suppression properties, but are less volatile at high temperatures. In the case of Polyvinyl Chloride (PVC), some results were obtained earlier (Ushkov et al. 1988, Carty 1996).

## 2 EXPERIMENTAL SETUP

We examined the thermal stability, combustion and smoke formation of composites based on several carbonizing polymers. Ferrocene according to RU TC 6-02-964-78 and its different derivatives

Table 1. Ferrocene and synthesized ferrocene derivatives.

Compound/abbreviation	Chemical formula	Amount of iron, % by mass	Molecular mass
Ferrocene/FEC	(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Fe	30.12	186
Oxyethylferrocene/OEF	C <sub>5</sub> H <sub>5</sub> FeC <sub>5</sub> H <sub>4</sub> -C <sub>2</sub> H <sub>4</sub> -OH	24.53	230
Acetylferrocene/AF	C <sub>5</sub> H <sub>5</sub> FeC <sub>5</sub> H <sub>4</sub> -CO-CH <sub>3</sub>	24.12	228
Diacetylferrocene/DAF	(C <sub>5</sub> H <sub>4</sub> -CO-CH <sub>3</sub> ) <sub>2</sub> Fe	20.28	271
Ferrocenedicarboxylic acid/FDA	(C <sub>5</sub> H <sub>4</sub> -COOH) <sub>2</sub> Fe	20.38	275
Copolymer of acryloyl ferrocene and isoprene/PAIF	-[C <sub>5</sub> H <sub>5</sub> FeC <sub>5</sub> H <sub>4</sub> -CO-CH-CH <sub>2</sub> ] <sub>n</sub> -[CH <sub>2</sub> -C <sub>3</sub> H <sub>4</sub> -CH <sub>2</sub> ] <sub>m</sub> -	9.62	~105
Polydiisopropenyl ferrocene/PDPF	$-[(C_5H_4-C-(CH_3)_2)_2Fe]_n-$	20.98	~105

(Table 1), which were synthesized and characterized in the laboratories of INEOS RAS, are used during an investigation.

Thermal stability, fire resistance and limiting oxygen index are studied for several types of polymer-based material that are widely used in the construction industry, which include: plasticized PVC (PPVC) and disperse-filled Epoxy Composites (EC). The latter type of composite is usually the subject of the so-called nanomodification process; the resulting nanocomposites with elevated operational properties can be successfully used for constructions operating in aggressive environments (Korolev 2012). Because of this, improvement of fire safety of EC is an important objective in construction. Epoxy oligomer ED-20, diabase and andesite powders are used as the matrix material and fillers for the investigated EC. Amounts of the filler and the admixture were 35% and 0.29%, respectively. Thermal stability of synthesized ferrocene derivatives and polymers was determined by means of thermogravimetry with an automated thermal-analytical complex DuPont-9900. Dynamic heating modes in air and nitrogen flows are used. Heating rates were 10 and 20 °C/min for air (during the determination of weight loss) and nitrogen (during thermal analysis), respectively. Several criteria of thermal stability, fire resistance and smoke formation are taken into account during the examination of fire rating, including: temperature  $T_{\rm bc}$  corresponding to the beginning of intensive decomposition, temperature  $T_{10}$  of 10% weight loss and temperature  $T_{\text{max}}$  of the maximal decomposition rate; rates  $R_1$  and  $R_2$  of decomposition at the first and second stages of the standard test; weight loss  $\Delta W_{600}$  at 600 °C; thermal effect of decomposition  $\Delta E$ ; Limiting Oxygen Index (LOI); ignition  $(T_i)$  and auto-ignition  $(T_{ai})$  temperatures; smoke formation factor  $(S_f)$  in pyrolysis and combustion modes. The aforementioned parameters are determined according to RU GOST 12.1.044. Eligibility of piecewise-sigmoidal models for the statistical description of experimental data

(Korolev et al. 2009) is determined by the regression analysis of preliminary results.

#### 3 RESULTS AND DISCUSSION

Obviously, combustion and smoke formation of polymer composites are related to the admixture properties. The results for the thermal stability of ferrocene derivatives are summarized in Table 2.

As can be observed from Tables 1 and 2, compounds with high molecular mass (PAIF and PDPF) are significantly less volatile at temperatures below 300 °C. As a rule, the low melting point corresponds to the low temperature of volatility; the dependence between the temperature of volatility and the rate of weight loss is not so clear. The matrix of correlation coefficients for columns of Table 2 is represented as follows:

$$r_{ij} = \begin{pmatrix} 1 & 0.95 & 0.46 \\ 0.95 & 1 & 0.18 \\ 0.46 & 0.18 & 1 \end{pmatrix}.$$
 (1)

The tight linear dependence between a melting point and the temperature of volatility is reflected by the  $r_{12}$  element, which is very close to the unit value.

On the contrary,  $r_{13}$  and, especially,  $r_{23}$  are considerably smaller; it can be shown that  $r_{23}$  is statistically insignificant at the 95% level of confidence. Thus, a high temperature of volatility not always corresponds to a low rate of weight loss. In fact, while the OEF should be considered as the most volatile derivative (weight loss starts at 128 °C), it is also characterized by a low rate of weight loss.

It is revealed that the chemical structure and the contents of ferrocene and its derivatives have a considerable impact on the heat resistance and LOI of the examined EC at high temperatures (Table 3). At low temperatures, ferrocene derivatives do not significantly affect the decomposition of epoxy composites ( $T_{\rm bc} = 273-285$  °C,  $T_{\rm max} = 300-306$  °C).

Compound	Melting point, °C	Temperature of volatility, °C	Rate of weight loss, %/min
OEF	75	128	12.5
AF	85	100	25.8
DAF	128	157	27.9
FDA	240	219	77.8
PAIF	250	314	26.5
PDPF	300	340	29.9

Table 3. Properties of EC with ferrocene derivatives.

	Values for different admixtures					
Parameter	Ref.	FEC	OEF	AF	FDA	PDPF
T <sub>ai</sub> , ℃	515	490	470	480	480	480
$R_1, \%/\min$	19.9	19.9	20.0	21.2	18.4	21.4
$R_2, \%/\min$	18.9	24.2	24.5	20.8	18.8	16.0
$\Delta W_{600}, \%$	65.7	67.7	59.1	64.3	59.4	67.7
$\Delta E$ , kJ/kg	4070	4300	3960	4300	4300	3300
LOI, %	23.3	27.6	28.3	25.6	26.1	25.8

The maximal rate of decomposition at the first stage is near to 20%/min.

The results of the examination of smoke formation for EC are summarized in Table 4.

The data presented in Tables 3 and 4 are in good agreement with the previously known fact that ferrocene and its derivatives can decrease only some of the parameters related to flammability, fire resistance and smoke formation, but not all of them.

In some cases, when the rate of decomposition is high, the high degree of carbonization (high weight loss) corresponds to high LOI (impeding candle-like combustion, FEC). In other cases, the high degree of carbonization corresponds to the low rate of weight loss and, at the same time, to the low LOI (PDPF).

As can be observed from Table 4, the ferrocene derivatives synthesized are superior smoke suppressors for epoxy composites. DAF is the most effective suppressor in the pyrolysis mode (smoke formation reduced to 51% of unmodified EC, 19% better than for FEC), and OEF is the best choice for the combustion mode (smoke formation reduced to 40%, 13% better than for FEC).

As before, the entire Table 3 can be represented by a matrix of correlation coefficients (Table 5).

As it follows from Table 5, for epoxy composites with ferrocene derivatives, there is a substantial positive linear correlation between:

- autoignition temperature and degree of carbonization ( $r_{14} = 0.48$ );

Table 4. Smoke formation of EC with ferrocene derivatives.

S <sub>f</sub> during pyrolysis, m²/kg	$S_{\rm f}$ during combustion, m <sup>2</sup> /kg	
1030	890	
720	480	
640	315	
520	410	
540	360	
	<i>S</i> <sub>f</sub> during pyrolysis, m <sup>2</sup> /kg 1030 720 640 520 540	

Table 5. Correlation coefficients for the properties of EC.

r <sub>ij</sub>	$T_{\rm ai}$	$R_1$	$R_2$	$\Delta W_{\rm 600}$	$\Delta E$	LOI
T <sub>ai</sub>	1	-0.11	-0.23	0.48	0.15	-0.77
$R_1$	-0.11	1	-0.19	0.59	-0.55	-0.1
$R_2$	-0.23	-0.19	1	-0.27	0.55	0.69
$\Delta W_{600}$	0.48	0.59	-0.27	1	-0.32	-0.33
$\Delta E$	0.15	-0.55	0.55	-0.32	1	0.07
LOI	-0.77	-0.1	0.69	-0.33	0.07	1

- decomposition rate at the first stage of the test and the degree of carbonization ( $r_{24} = 0.59$ );
- decomposition rate at the second stage of the test, the thermal effect of decomposition and the oxygen requirement for candle-like combustion.

At the same time, a high LOI corresponds to the low autoignition temperature ( $r_{16} = -0.77$ ). The observed peculiarities can be attributed to the increased decomposition rate of the condensed phase, which, in turn, is caused by iron oxides formed during the decomposition of ferrocene derivatives. The latter is consistent with the results reported previously (Dyagileva 1979). In the presence of ferrocene derivatives, the LOI of EC increases from 23.3 to 25.6-26.1%. Higher values of LOI (28.3%) are observed for composites containing OEF. It is also found that while ferrocene derivatives lower  $T_{ai}$  by 20–35 °C, they have a little effect on  $T_i$  (which is nearly 225 °C for all studied EC). The results confirm that the effect of ferrocene derivatives is mostly on the hightemperature region of EC.

The increase in the concentration of ferrocene derivatives corresponds to the decrease in EC flammability. Significant improvement of LOI is observed for compositions containing OEF (Fig. 1): when the concentration is raised from 0.17 to 1.71%, the LOI increases from 23.4 to 28.9%.

In our opinion, ferrocene derivatives contribute to the formation of the carbonized barrier layer on the surface of the burning material. This layer



Figure 1. LOI of EC with different ferrocene derivatives: 1—OEF; 2—FEC; 3—DAF; 4—FDA; 5—AF.

induces the penetration of volatile products from pyrolysis, and prevents heat and mass transfer and further spread of the flame. An essential increase of LOI is observed when the concentration of ferrocene derivatives is higher than 0.6%. At the same time, the concentration of ferrocene derivatives does not correlate with  $T_i$  but negatively correlates with  $T_{ai}$ . The increase in DAF concentration ranging from 0.17 to 1.7% reduces  $T_{ai}$  from 505 to 490 °C.

Due to revealed peculiarities, there can be complications during the selection of the appropriate admixture for fire-safe EC.

We also examined the smoke formation, thermal and fire resistance of PPVC with admixtures of ferrocene derivatives. The results are summarized in Table 6 and Figure 2.

The presence and type of ferrocene derivatives do not have a significant effect on either the characteristic temperatures for PVC materials or the dehydrochlorination processes and decomposition in the air. Weight loss during the standard test is 64.5–67%.

It is evident from Figure 2 that for higher concentrations of ferrocene derivatives (up to 0.7%), the LOI of the PVC increases from 30 to 36.8%. The smoke formation factor in the pyrolysis and combustion modes can be reduced from 925 and 660 to 710 and 350 m<sup>2</sup>/kg, respectively. As with EC, the ferrocene derivatives are more effective admixtures for PPVC than pure ferrocene. The higher efficiency of AF and OEF compared with pure ferrocene is due to their active decomposition that leads to the formation of ultrafine catalytically active iron oxides. Such oxides form a barrier layer on the surface and inhibit the formation of smoke. The optimum concentration of ferrocene derivatives in PVC materials is 0.3–0.5%.

### 4 SUMMARY AND CONCLUSION

In the present work, we summarized and discussed the results of several laboratory tests. The tests were

Table 6. Properties of PPVC with ferrocene derivatives.

Parameter	Values for different admixtures				
	Ref.	FEC	AF	OEF	
$ \begin{array}{c} T_{\rm bc} \\ T_{10} \\ T_{\rm max} \\ T \end{array} $	240 260 285 420	240 255 280 420	245 260 285 420	247 263 290	



Figure 2. Dependencies of LOI (1, 2, 3) and smoke formation factor in pyrolysis (1', 2', 3') and combustion mode (1'', 2'', 3'') for PPVC: 1—FEC; 2—OEF; 3 – AF.

carried out to answer the question concerning the suitability and effectiveness of ferrocene and its derivatives as admixtures for fire-safe construction.

It is discovered that ferrocene derivatives of relatively low volatility can be successfully used as efficient smoke suppressors and fire retardants during the production of polymer composites for fire-safe construction. For epoxy composites, the application of diacetylferrocene and oxyethylferrocene reduces smoke formation by 49% and 60% in the pyrolysis and combustion modes, respectively. However, it is again confirmed that probably no universal chemical agent allows increasing all operational properties related to fire safety at once. Examined admixtures provide low weight loss, slow rate of decomposition, high LOI and low smoke formation factor, though optimal values of these parameters cannot be simultaneously reached at any single point in factor space.

#### ACKNOWLEDGMENTS

This work was supported by the Ministry of Science and Education of Russian Federation, Project # 7.2200.2014/K "Nanomodified polymer composites for fire safe construction".

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