Development of led-curable intumescent polymer coatings for fire protection of building constructions

A Tomakhova, O Zybina, V Suprun and O Babkin
Peter the Great St.Petersburg Polytechnic University, St.Petersburg, Russia, University of Leipzig, Leipzig, Germany, St. Petersburg State University of Film and Television, St.Petersburg, Russia

E-mail: ozakata@mail.ru

Abstract The influence of reactive monomer on the properties of fire-protective intumescent composition and the final UV-curable coating was investigated; it was established that compositions based on isobornyl acrylate, mixture of hydroxyethyl methacrylate with dipropylene glycol, and cyclohexyl methacrylate form charred layers with sufficient fire-protective and mechanical properties.

Keywords: fire protection, polymer coatings, building constructions, safety.

1 Introduction
Fires are a part of a short list of preventable disasters. This is why any events which purpose is to prevent fires and stop their spreading are so important. The bulk of building constructions and materials must be protected from fire. Intumescent compositions are widely used for this purpose nowadays; such compositions form a heat-isolating carbonaceous foam on the objectives surface when it's exposed to high temperatures. This foam, called a charred layer, increases constructions fire resistance.

Intumescent compounds include such basic components as pentaerythritol, melamine and ammonium phosphates (mostly high-condensed ammonium polyphosphate) [1,16]. These components react in a following order: pentaerythritol thermally decays and forms formaldehyde and acetaldehyde, which in their turn react with melamine and form the frame of a future charred layer melamine-aldehyde resin. The resin gets swelled under the influence of gaseous side-products of condensation, and after that cures with ammonium polyphosphate as a catalyst. It is important to make a correct composition so that its components could support a process of thermolytic synthesis of a charred layer (fig. 1).

![Figure 1. Charred layer on a surface](image-url)
Nowadays there is a need in fast-drying (curing) materials. LED-curable intumescent fire retardant materials may be an answer to these needs. One of the advantages of such materials is that they can be applied to a construction/detail outside the construction site. They can be also applied to small-sized details or building elements which must be fire retardant.

LED-curing process is based on the ability of ultraviolet radiation to start the reaction of cross-linking in oligomeric materials with special chemical structure. The energy of ultraviolet radiation is quite high 3.1-12.4 eV; C=C link (which has an energy of 6.3 eV) allows hardening the coatings with acceptable speed and at normal temperatures.

Polymer binder has a big influence on the structure of a forming charred layer it has to be isotropic, heat resistant tough foam. A polymeric matrix must decay before the start of thermolytic synthesis of a framing resin, so that the intumescent effect could be acceptable. Due to this, the most complicated for development are the compounds based on polymers which form a spatial structure (epoxides, polyurethanes). Polymer binders which are able to harden under UV radiation are epoxyacrylates, epoxy-ether acrylates, poly-ether acrylates, unsaturated polyesters, urethaneacrylates [2,17].

The purpose of current research was to investigate the way of how a reactive monomer impacts the properties of an intumescent composition; in particular how do the functionality, glass transition temperature, polarity/nonpolarity (hydrophilicity/ hydrophobicity) of monomers, and also their quantities in a compound, impact the properties of an intumescnt composition and the coating formed from it.

2 Materials and methods
Low molecular weight oligomer, reactive diluent, photoinitiator, synergist, fillers and pigments were included in a basic LED-curable fire retardant composition. Oligomers type determines protective and physico-mechanical properties of a composition. Reactive diluent (monomer) is a component which takes part in coatings formation and impacts the viscosity of a composition. Photoinitiator determines the portion of LED radiation which is needed for hardening. The intumescent system which is responsible for a charred layers formation is a mixture of ammonium polyphosphate, melamine and pentaerythritol (3:1:1). Five monomers of different functionality were chosen as chemicals with C=C links. 10 mas.% of photoinitiator were used. [4,18].

18 compositions were prepared using the basic one (table 1). They were identical, only monomers were different (table 2). Monomers which were used in compositions: isobornyl acrylate (IBOA), hydroxyethyl methacrylate (HEMA), cyclohexyl methacrylate (CHMA), dipropylene glycol diacrylate (DPGDA), trimethylpropane triacrylate (TMPTA). Compositions were prepared by mixing the components during 20 min at normal temperature; then they were applied to steel plates using 300 µm applicator and cured using LED radiator (coating forms during ~1 min when radiation power is 300 W). Coatings thickness was measured using thickness gauge «Konstanta K5» (ISO 2808).

| Component                                           | Quantity, mas.% |
|-----------------------------------------------------|-----------------|
| Photoinitiator                                      | 5               |
| Oligomer                                             | 1               |
| Intumescent triad (pentaerythritol, melamine, ammonium polyphosphate) | 50              |
| Monomer                                             | 44              |
| Total                                               | 100             |

Table 2. Monomers used in compositions.

| №  | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 |
|----|---|---|---|---|---|---|---|---|---|----|----|----|----|----|----|----|----|----|
|    |   |   |   |   |   |   |   |   |   | 18 |    |    |    |    |    |    |    |    |
Steel plates with applied intumescent compositions were exposed to annealing in a furnace (at 600 °C) (fig. 2) during 5 minutes; swelling coefficients of coatings was measured and compared with an initial sample.

|  |  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  |  |  |  |  |
| IBOA | 4 | - | - | - | 41 | 37 | 33 | - | - | - | - | 41 | 37 | 3 | - |
| 4 | .8 | 4 | .0 | 1 | 2 | 4 | .8 | 4 | 3, | 1 | 2 | 0 | .4 | - |
| HEMA | - | 4 | - | - | - | - | - | 41 | 37 | 33 | - | - | - | - | 41, |
| 4 | .8 | 4 | .0 | 1 | 2 | 4 | 81 |
| CHMA | - | 4 | - | - | - | - | - | - | 41 | 37 | 33 | - | - | - | - |
| 4 | 1 | 2 | 4 |
| DPGDA | - | - | 4 | 2, | 6, | 10 | 2, | 6, | 10 | 2, | 6, | 10 | - | - | - |
| 4 | 19 | 58 | .9 | 19 | 58 | .9 | 19 | 58 | .9 |
| TMPTA | - | - | 4 | - | - | - | - | - | - | 2, | 6, | 1 | 2,1 |
| 4 | 19 | 58 | 0, | 9 |
| 9 |

Swelling coefficient was measured using the following formula:

K= h/h0,
h charred layers thickness, mm;
h0 initial layers thickness.
This method is quite informative and reproductive [5,6].

3. Results
Compositions were studied after annealing in a furnace (table 3). Compositions which performed the best included monomers with large substitute (table 4). Such substitute ensures the formation of a tough polymer matrix which does not hinder the process of thermolytic synthesis. Compositions based on isobornyl acrylate and hydroxyethyl methacrylate with dipropylene glycol show the highest swelling coefficient; the lowest one is shown by composition based on cyclohexyl methacrylate.
Table 3. Results of fire tests of compositions № 15, №1, №3 and №9.

| №  | Initial layers thickness, mm | Charred layers thickness, mm | Swelling coefficient | Time of reaching the critical temperature (500 °C), min | Commentaries                                      |
|----|-----------------------------|------------------------------|----------------------|-------------------------------------------------------|---------------------------------------------------|
| x  | 0,15                        | Coating did not cover the substrate | –                    | 6                                                     | Structure with large cells, tends to form smaller ones |
| 1  | 0,15                        | 6,06                         | 40,58                | 16                                                    | Structure with large cells                         |
| 3  | 0,17                        | 2,7                          | 15,55                | 12                                                    | Structure with small cells                          |
| 9  | 0,13                        | 4,9                          | 37,44                | 15                                                    | Structure with large cells                          |

Table 4. Monomers comparison.

| Properties                      | IBOA          | CHMA         | DPGDA         |
|---------------------------------|---------------|--------------|---------------|
| Chemical name                   | Isobornyl acrylate | Cyclohexyl methacrylate | Dipropylene glycol diacrylate |
| Formula                         | ![](https://latex.codecogs.com/png.latex?\text{H}_2\text{C}\cdot\text{CH}_3) | ![](https://latex.codecogs.com/png.latex?\text{O}\text{CH}_2\text{O}) | ![](https://latex.codecogs.com/png.latex?\text{H}_2\text{C}\cdot\text{CH}_2\text{O}-(\text{CH}_2\text{O})_2\text{CH}_2\text{CH}_3) |
| Functionality, -C= C-           | 1             | 1            | 2             |
| Molecular mass, g/mole          | 208           | 168.23       | 250           |
| Glass transition temperature, C° | 88-94         | 92-110       | 102-104       |

Compositions based on isobornyl acrylate show the best charred layers structure and sufficient spreading on a substrate (fig. 3).

![Figure 3. Sample after annealing.](image-url)
4. Discussion
It was detected that different samples form charred layers with different toughness and isotropy depending on the type of a polymer binder. The best properties were shown by composition based on isobornyl acrylate. This may have a connection with the carbon structure formed in the process of pyrolysis. It was established, using X-ray crystallography, that compositions based on hydroxyethyl methacrylate and cyclohexyl methacrylate tend to form structures similar to one of an amorphous carbon; it's shown by a wide diffraction peak. Composition based on isobornyl acrylate shows a peak at 22°C (fig. 4) which is a sign of formation of locally ordered polyaromatic carbon.

![Figure 4. Diffractogram of char formed from composition based on isobornyl acrylate (t, 600 °C).](image)

Such structures may act as catalysts in the process of thermolytic synthesis of a charred layer thus ensuring better properties of supramolecular polymer structure of a charred layer.

Intumescent compositions based on polymers with spatial structure often show low values of swelling coefficient. Such compositions neither form heat-isolating charred layer nor cover the substrate with it (Fig. 5). This became true for the compositions which we prepared using monomers of dipropylene glycol and trimethylpropane. Sufficient properties were shown by three samples based on isobornyl acrylate, mixture of hydroxyethyl methacrylate with dipropylene glycol, and cyclohexyl methacrylate. Compositions №1, №3 and №9 show sufficient results which is because they include spatial substitutes; they prevent formation of an empty polymer web while curing, thus empowering an intumescent effect.

![Figure 5. Samples after fire tests; charred layer did not cover the substrate.](image)
5. Conclusion
According to obtained experimental data it can be stated that UV-curing technologies are usable for development of fire-retardant polymer coatings. Sufficient fire-protective properties were shown by compositions including monomers with one double bond (isobornyl acrylate, cyclohexyl methacrylate) and monomers with single-double bonds (hydroxyethyl methacrylate with dipropylene glycol). Changing the initial LED-curable composition allows to regulate the properties of forming charred layers.

We have developed the basic fire retardant LED-curable composition. It was established that isobornyl acrylate is the most preferable monomer for this kind of compositions.

References
[1] Camino C, Costa L, Martinasso G 1989 Intumescent fireretardant systems Polymer Degradation Stability №23 p 359-376.
[2] Burlov V, Popov N 2017 Management of the application of the space geoinformation system in the interests of ensuring the environmental safety of the region Advances in the Astronautical Sciences
[3] Bardin A, Korotkov A, Kazarnovskij V 2017 Limit of fire resistance of a steel transport structures. Simplified calculation methods IOP Conference Series: Earth and Environmental Science, 90 (1) DOI: 10.1088/1755-1315/90/1/012207
[4] Bourbigot S, Le Bras M, Duquesne S, Rochery M 2004 Recent advances for intumescent polymers Macromolecular Materials and Engineering No289 pp 499-5.
[5] Wang, Z. Fire-retardant effect of nanoclay on intumescent nanocomposite coatings/Wang, E. Han, W. Ke//Journal of Applied Polymer Science. 2007. №103. –P..-681–1689
[6] Babkin O E, Babkina L A, Nenovski A G, Proskuryakov S V, Silkin A Yu Effect of an active diluent on the protective coating of UV-curing // Paintwork materials and their application. 2012. No. 7. P. 42-46.
[7] A method for improving the adhesion strength of UV-curable polymer compositions to metal / O.S. Aykasheva, O.E.Babkin, L.A. Babkina, A.G. Esenovskii, S.V. Proskuryakov, 2012 Polymer Science Series D.
[8] Mikhailova D, Bulgakov V, Tolpeksa N A 2011. Otsenka kachestva ognezashchity i ustanovleniye vida ognezashchitnych pokrytij na ob*yektakh: Rukov Duderov, Ye M.:MCHS Moskva, p 26
[9] Pagella C, Rafiaghello F 1998 Differential scanning calorimetry of intumescent coatings Paint Colour Journal. Vol. 188, № 4402 pp 16-18.
[10] Ustinov A, Zyibina O, Tanklevsky L, Lebedev V., Andreev A 2018 Intumescent coatings with improved properties for high-rise construction E3S Web of Conferences 33, 02039 https://doi.org/10.1051/e3sconf/20183302039.
[11] Gravit M, Gumerova E, Bardin A, Lukinov V 2018 Increase of Fire Resistance Limits of Building Structures of Oil-and-Gas Complex Under Hydrocarbon Fire Advances in Intelligent Systems and Computing. 692 pp 818-829 DOI: 10.1007/978-3-319-70987-1_87
[12] Korshunov G, Polyakov S, Shunmin L 2017 Assurance of reliability and safety in liquid hydrocarbons marine transportation and storing IOP Conference Series: Earth and Environmental Science, 87 (6) DOI: 10.1088/1755-1315/87/6/062009
[13] Burlov V, Andreev A, Gomazov F 2018 Somga-Bichoga, N. System integration of security maintenance processes in knowledge management Proceeding of the European Conference on Knowledge Management, ECKM
[14] Burlov V, Grachev M, Shlygina S. 2017 Adoption of management decisions in the context of the uncertainty of the emergence of threats Proceeding of 2017 20th IEEE International Conference on Soft Computing and Measurements SCM 2017 pp 107-108 DOI: 10.1109/SCM.2017.7970510
[15] Pykhtin K, Simankina T, Sharmanov V, Kopytova A 2017 Risk-based approach in valuation of
workplace injury rate for transportation and construction industry IOP Conference Series: Earth and Environmental Science 90 (1) DOI: 10.1088/1755-1315/90/1/012065

[16] Gravit M, Kuleshin A, Khametgalieva E, & Karakozova I 2017 Technical characteristics of rigid sprayed PUR and PIR foams used in construction industry. Paper presented at the IOP Conference Series: Earth and Environmental Science, 90(1) doi:10.1088/1755-1315/90/1/012187

[17] Gravit M V, Nedryshkin O V & Ogidan O T 2018 Transformable fire barriers in buildings and structures. Magazine of Civil Engineering, 77(1), 38-46. doi:10.18720/MCE.77.4

[18] Ustinov A, Zybina O, Tomakhova A & Pavlov S 2018 The enhancement of operating properties of intumescent fire-protective compositions. Paper presented at the MATEC Web of Conferences, 245 doi:10.1051/matecconf/201824511008