PULTRUSION COMPOSITES AND PRODUCTS WITH HIGH FIRE RESISTANCE ON THE BASE OF NANOMODIFIED POLYMERS IN BRIDGE ENGINEERING

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Introduction

In recent years we can observe the dynamic development of works regarding metal application in dispersive state for reduction of inflammability of organic substances, particularly, plastics and laminated plastics on its base [1, 2]. In this case the most appropriate metals are elements of cuprum subgroup (cuprum, gold, silver) which are placed below hydrogen in the row of stresses and are characterized as relatively short normal electrode potential of transfer into the state with low oxidation level. Meanwhile, such a tendency has been already realized in technics, for instance, application of lead tetraethyl in engine fuel for the reduction of burning rate (anti-detonator) or application of cuprum meshes in explosion-proof Devy lamps.
Aim of the present researches is to find the technology of nanocuprum injection into pultrusion resin and to examine the properties of produced pultrusion material.

Experimental

The combustion process is the complex of oxidation-reduction reaction. Active centers of reactions are radicals (primarily hydroxylic). That is why our approach to the reduction of combustion of composites consists in the reduction of chain processes. In this case it is possible to use various forms of cuprum compounds with decreased rate of oxidation (in comparison with usual rate of oxidation). Due to this we have examined two approaches of cuprum forms injection into the cured systems:

1. Synthesis of nanocuprum in resin. This gives the possibility to receive clusters or nanosized particles. This saves from necessity to protect them from oxidation and aggregation etc.
2. Prepared nanocuprum particles were injected into the resin.

General scheme of samples' receiving included the following processes:

1. Receiving of molecular solution of cuprum formulations. The main requirements to these systems are:
   - Good solubility. Solution should be compatible with the resin and not to precipitate at curing.
   - Solution should not inhibit the reaction of curing.
   - Solution shouldn't decrease the Tg of the cured resin
   - Solution should be feasible for using it in different resins (polyether, epoxy and etc.)
2. Curing of resins.
3. Regeneration of cuprum compounds in cured resins, in other words, in conditions of matrix isolation.

In accordance with accepted scheme and in case of following of mentioned above the requirements there have been received the samples of cured resin. Moreover, the content of cupric chloride and reducing agent has been varying. Reaction of styrene polymerization was used for comparison.
It is obvious, that maximum effect of fireproof is achieved for polystyrene and it is substantially lower for the two examined resins. Maximum effect of fireproof is achieved at narrow interval 0,2-0,5% of nanocuprum content (in conversion to initial salt).
In accordance with the second approach, there has been received the resin on the base of vinyl ether resin. Cuprum nano-particles, in vacuum isolation under the intensive agitation with the help of ultrasound, were injected into resin. Nano-particles were encapsulated before. This prevents the process of oxidation.
On the base of the resin, modified with nanocuprum there have been produced profiles (U-profile 400x120x18mm) reinforced with glass fibers (Picture 1). The samples have been tested in accordance with 2 methods:

- Method of vertical tube
- Standard method which is used for the evaluation of construction materials' fire resistance.

Fig.1: Glass fiber U-profile 400x120x18mm on the base of vinyl ether resin with nanocuprum

Research of combustibility, thermo physical properties and structure of glass fiber

With the help of DSK method it was evaluated the glass transition temperature of the U-profile material. Tg of the material decreased on 12°C in comparison with the check sample without cuprum.

By electron microscopy method there has been examined the structure of glass fiber samples which were cut from the U-profile.

For maintaining of proportional dispersion of heavy particles it's necessary to apply the surface-active compound or to organize uninterrupted resign barbotage in bath during pultrusion.

It was determined the fire resistance of fiberglass U-profile sample with nanocuprum by "vertical tube" method. The method consists of the following. The burner flame should be carried to the vertically suspended free extremity centre of sample. Ignition time and time of self-contained burn after burner taking away is recorded. The weight of cold sample is defined.

Not easy combustible materials are materials, which lose less than 20% of the organic component and self-contained burn less than 30 seconds after burner taking away; self-extinguishing materials are materials, which lose less than 8% of organic component and extinguish immediately; incombustible material are materials, which do not catch fire within 2,5 minutes after two ignition.

At analyzing the test results and samples condition is defined, that the samples are initiated on 150th second, at taking away from the fire they extinguish on 4th ,7th ,21st second, they have minimum lost of weight 0,4-0,6 %, they do not flake away in combustion zone and smoke a little bit.

Burning is generally on the side and doesn't penetrate deep into the sample.

In the Table 1 are shown the results of combustibility and inflammableness determination in accordance with the building standards. From the following results it can be seen, that within the flammability tests all the values practically decline, particularly one of the most important -temperature of the smoke fume. At inflammability test a critical surface density of rate, which the sample can bear, has raised on 25 %.

Table 1

Designation	Without nanocuprum	With nanocuprum
Combustibility State Standard 30244-94		
Temperature of smoke fumes , °C	184	105
Time of self-contained burn, from	29	26
Sample damage along the length, %	15	12
Sample damage degree in mass	2	1
Inflammableness State Standard 30402-96		
Time before inflammation if heat-flow rate, from: – 20 kVt/m^2 – 25 kVt/m^2 – 30 kVt/m^2	600 - 154	none 911 391
Critical surface density of heat-flow rate, kVt/m^2	20	25

Conclusion

1. In accordance with the research results, which have been conducted on the model samples, it has been defined prohibitive amount of the cuprum for the resin modification on the basis of vinyl ether and epoxy resin.
2. There has been selected the conditions for the U-profile production 400x120x18 on the basis of resin with insertion of nanocuprum.
3. During test result analyses there has been found out, that for material samples with nanocuprum has been achieved improvement of all burning and ignition values in comparison with model samples.

References:

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