[Research Paper]

캡슐화된 소화약제의 물성에 대한 고분자 매트릭스의 효과

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The Effect of Epoxy Resin on the Properties of Encapsulated Fire Extinguishing Agent

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요 약

저점도 에폭시 수지(EP)를 기본으로하고 캡슐화된 소화약제(EFA)를 50 wt%의 함유한 소화복합재료가 얻어졌다. 탈캡슐화된 EFA의 동역학 및 온도에 대한 EP의 긍정적인 효과가 확립되었다. EP는 EFA의 탈캡슐화 온도를 130 ℃에서 155 ℃로 증가시키고 캡슐화의 역학을 변화시킨다. 에폭시 매트릭스는 순수한 EFA와 비교하여 EFA의 열 안정성을 3.9배 이상 증가시킨다. EFA의 저장 안정성에 대한 EP의 보호 효과가 발견되었다. 60 ℃ 및 80% 습도에서 96시간 동안 EFA를 함유하는 EP의 질량 손실은 0.4%이고, 동일한 조건에서 순수한 EFA의 질량 손실은 15%이다. 자외선의 영향 아래에서 EP의 동일한 효과: 순수한 EFA가 6%인 경우 EFA를 함유한 EP는 0.8% 손실된다. 대안의 중합체매트릭스의 시험이 고려되었다.

ABSTRACT

Fire extinguishing composite materials based on low-viscosity epoxy resin (EP) and containing 50 wt% of encapsulated fire extinguishing agent (EFA) have been studied. The positive effect of the EP on the kinetics and temperature of the EFA decapsulation was established. The EP increases the decapsulation temperature of the EFA from 130 $^{\circ}$ C to 155 $^{\circ}$ C and changes the kinetics of the decapsulation. The epoxy matrix increases the thermal stability of the EFA more than 3.9 times compared to that of the pure EFA. The protective effect of the EP on the storage stability of the EFA was validated. The mass loss of EP-containing EFA at 60 $^{\circ}$ C and 80% humidity over 96 h is 0.4%. The mass loss of pure EFA under the same conditions is 15%. A similar effect was observed under ultraviolet radiation: the EP-containing EFA loses 0.8% at pure EFA mass of 6%. The testing of alternative polymer matrixes has been considered.

Keywords: Perfluoro (2-methyl-3-pentanone), 3MTM NovecTM1230, Encapsulated fire extinguishing agent, Fire extinguishing composite

1. Introduction

Firefighting methods and devices in the early stages of a fire in confined spaces is an actual problem⁽¹⁾. This problem is especially relevant in the field of microelectronics and electric power industry⁽²⁾, in particular in large-capacity energy storage devices⁽³⁾, batteries for electric vehicles and other devices

where lithium-ion batteries (LIB) are used^(4,5). The above articles indicate a large list of products subject to ignition - from small consumer electronics to large electric vehicles and airplanes. Although various safety devices have been incorporated into the commercial LIB cells, there have been numerous high-profile battery failure accidents, many of which caused significant adverse impacts for the cell manufacturers

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as well as companies utilizing LIB technology within their products⁽⁴⁾.

At the moment, there is a number of publications referring to research projects aimed at solving this problem. Among the main ways to prevent the combustion of LIBs are noted: using of battery management system⁽⁶⁾, thermal management system⁽⁷⁾, battery protected boxes⁽⁴⁾, pressure release in battery pack as well as the use of new materials^(8,9). The use of encapsulated fire extinguishing agent with low boiling temperature (EFA) is one of the solutions to the safety problem of such devices⁽¹⁰⁾. Perfluoro (2-methyl-3-pentanone) (FK-5-1-12, 3MTMNovecTM1230) is one of the most promising agents⁽¹¹⁾. It is aligned with the Montreal Protocol and is a liquid under normal conditions^(12,13).

In⁽¹⁴⁾ authors propose a method for producing an EFA. It is a core@shell structure and the core material is perfluoro (2-methyl-3-pentanone). However, the authors state a low decapsulation rate and temperature, as well as a high mass loss when exposed at temperatures above the boiling point of the core material. These problems create limitations for the subsequent use of this EFA. The reason for this may be low mechanical strength of the shell, high porosity of sell's material and his hydrophilicity, as well as high content of gaseous products of hydrolysis of perfluoro (2-methyl-3-pentanone) in the core.

Problem of low decapsulation rate and temperature can be solved in two ways. The first is the change in the properties of EFA by changing the synthesis mechanism^(15,16) and the properties of the material shell⁽¹⁷⁾. The shell significantly affects the decapsulation process of EFA in a narrow time and temperature range. The second is the adding of EFA into a polymer matrix to obtain fire extinguishing composite materials⁽¹⁴⁾.

This paper describes the second option. In particular, the effect of the type of polymer matrix on the decapsulation temperature, its kinetics, and the tightness of the resulting fire extinguishing composite materials. This article describes the effect of the polymer matrix on the decapsulation rate, decapsulation temperature and thermal stability, which was evaluated according to the thermogrametric analysis as well as stability under prolonged exposure to UV radiation. The main goal is to compare the properties of pure EFA and composite materials based on them. In addition, the selection of the matrix for the manufacture of composite materials, the choice of mold material, as well as the thermomechanical properties of the obtained composite materials are analyzed.

Experimental

2.1 Encapsulated fire extinguishing agent (EFA) Encapsulated fire extinguishing agent produced by GFI Co.

Ltd. It was used to make samples of fire extinguishing composite materials. EFA is a core@shell structure. The core material is perfluoro (2-methyl-3-pentanone) $3M^{TM}Novec^{TM}1230$ and shell is a solid non-porous polymeric material. The EFA's capsules size is in the range of 150-350 microns. The decapsulation temperature is 130 $^{\circ}$ C.

2.2 Preparation of fire extinguishing composite materials

YD-115 epoxy resin (Kukdo Chemical Co. LTD) and KH-819 epoxy resin hardener (Kukdo Chemical Co. LTD) were used to obtain samples of fire extinguishing composite materials. In accordance with Technical Data Sheet (TDS), 34.3 g of YD-115, 15.7 g of KH-819 and 50 g of EFA were used to produce 100 g sample. The mass concentration of the EFA in the resulting composite material was 50%. The components were sequentially loaded into the mixer, mixed for 5 min, then the resulting mass was evacuated for 10 min to remove the air captured during mixing. Sheet-shaped samples (2-4 mm thickness) were made by casting on a base. Rod-shaped samples for dilatometry analysis were made by injection molding.

2.3 Characterization

2.3.1 Thermograyimetric Analysis

Thermogravimetric analysis (TGA) of samples of composite materials was carried out by Netzsch TG 209 F3 Tarsus thermomicrobalance. In this work, the analysis was carried out by two methods.

First one: monotonous heating of the sample from room temperature to the complete end of the decapsulation process. The purpose of the test was to determine the decapsulation temperature of EFA and compositions containing EFA, the peak speed of this process, and the mass loss due to heating. The analysis parameters are shown in Table 1.

Second one: isothermal exposure of samples at 60 $^{\circ}$ C, 80 $^{\circ}$ C and 100 $^{\circ}$ C for 24 hours. By this method were evaluated of the thermal stability of EFA and composite materials based on them. In other words, leakage tendency of the core material,

Table 1. TGA Parameters

Thermocouple Type	P Type
Crucible Material	Al
Heating Rate, K/min	10
Final Temperature, °C	300
Purge Gas	Synthetic Air

which determines by the tightness of the capsule shell material. In fact, thermal stability is a measure of the ability of a core material to leak from EPA or a composite material based on it. The results were used to evaluate the weight loss of the sample during testing. For a composite material containing 50% EFA by weight, the calculation was carried out with adjustment for its content in the matrix.

2.3.2 Dilatometry analys

Dilatometry analysis was performed on a thermomechanical analysis instrument Netzsch TMA 402 F3 Hyperion. The measurements were carried out in a dynamic nitrogen atmosphere, when the samples were heated from 5 $^{\circ}\mathrm{C}$ to 110 $^{\circ}\mathrm{C}$ at a speed of 5 K/min. Based on the measurement results, elongation and coefficient of thermal expansion (CTE) were evaluated.

2.3.3 Adhesion test

The adhesion of the cured composite material to the substrate materials were determined by pull-off adhesion method using the DeFelsko PosiTest AT-M Manual 20 mm Kit. It was measure the force required to completely detach dollies from the substrate material. 3 samples for each substrate were analyzed to obtain reliable data.

2.3.4 Fire extinguishing time determination

To determine the fire extinguishing time of composite materials containing EFA were used a special metal box with a polycarbonate door. It volume was 48 ℓ (dimensions is 30 \times 20 \times 80 cm). The box had holes in the side walls. Fuel (heptane) and a sample of fire extinguishing composite material were placed in a box at a distance of 30 cm from the source of fire. After that, the heptane was set on fire and the box door was tightly closed, simultaneously detecting the time of the beginning of the experiment. Time of complete extinguishing was determined during the experiment.

2.3.5 Climate test

Accelerated climate tests were performed in a DYI-TH-02 chamber (Dong Yang International Co. Ltd). The samples of EFA and composite materials containing EFA were exposed for 96 hours at 80% relative humidity and temperature from 25 °C to 60 °C. According to the results of climatic tests, the change in mass of the samples and fire extinguishing time were established. The calculation of the values of fire extinguishing time and mass lost were carried out according to the test results of 5 samples for each condition.

3. Result and discussion

3.1 Matrix selection

In this work various polymeric materials are analyzed and research to create a fire extinguishing composite material containing EFA. Polymer matrix requirements are formed:

The polymer is a thermoplastic, thermoset or elastomer, but it curing or melting temperature do not exceed decapsulation temperature of EFA.

The viscosity of molten or uncured polymer is not exceed 20,000 cps.

Polymer should allow to obtain highly filled compositions with filling up to 50-70% by weight.

Polymer is chemically inert to the shell of the EFA. It doesn't destroy microcapsules and ensures the complete absence of diffusion of liquid extinguishing agent to the environment.

The properties of the polymer are retained during long-term storage above the boiling point of a liquid fire extinguishing agent, at high humidity and under the UV radiation.

The polymer should increase the temperature and kinetics of decapsulation of EFA.

The method of producing the fire extinguishing composite doesn't include the use of shear stresses, pressures, etc.

An overview of the properties of the analyzed multi-ton polymer materials is shown in Table 2. Based on data on melting or glass transition temperature and state of aggregation are concluded that thermoplastics are not suitable for use as a matrix for EFA. Therefore, modified polyvinyl alcohol (MPVA), unsaturated polyester resin (UPR), polymethyl methacrylate/methyl methacrylate (PMMA) and epoxy resin (EP) are selected for the matrix.

3.2 The effect of EP on TGA

The Figure 1 shows the TG curves for various polymers containing 50 wt.% of EFA. PMMA and UPR reduce the temperature of EFA decapsulation to 64 °C and 106 °C, respectively. In addition, the gentle kinetics of the curve shows that the EFA slowly decapsulate over a wide range of temperatures. PMMA and UPR impair decapsulation kinetics of EFA. MPVA doesn't affect the temperature of EFA decapsulation. It remains in the range of 125 °C-135 °C. Only epoxy resin increase the temperature of decapsulation of EFA to 155 °C. High affinity of epoxy resin for the EFA shell material can explain this effect.

Moreover, the fire extinguishing time of the composite materials are analyzed. EFA are enclosed in an EP show a short fire extinguishing time (20 ± 3) s. Other composite ma

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Polymer	Melting	Glass Transition	Processing/curing	Shrinkage, %	State of Aggregation	Molecular
	Temperature, °C	Temperature $^{\circ}\mathbb{C}$ Temperature, $^{\circ}\mathbb{C}$		Sillilikage, 70	at 25 ℃	Weight, ×10 ³
Polypropylene	Polypropylene 160-176		160-260	1.3-2.4	Solid	60-300
D-1	240	90 100	160-240	0.3-0.6	Solid	00.100
Polystyrol	(Isotactic)	80-100				80-100
Low Density Polyethylene	105-115	-40- (-50)	200-260	1.5-2.0	Solid	30-400
High Density Polyethylene	130-140	120	220-280	1.5-2.0	Solid	50-1000
Acrylonitrile Butadiene Styrene	-	95-125	200-260	0.4-0.7	Solid	-
Polyethylene Terephthalate	255-265	95-100	270-280	0.2-2.0	Solid	20-50
	200	85		0.5.5.0	T:	20.50
Modified Polyvinyl Alcohol	(solid)	85 - 0.5-5.0		Liquid	20-50	
Unsaturated Polyester Resin	-	60-170	< 25	0.1-10	Liquid	-
Poly (Methyl Methacrylate)		45-115	< 40	0207	Liquid	0.1
	-	(solid)	<u> </u>	0.2-0.7		(MMA)
Epoxy Resin	-	50-200	< 25	0.1-0.5	Liquid	-

Table 2. Overview of the Main Properties of Polymer Material

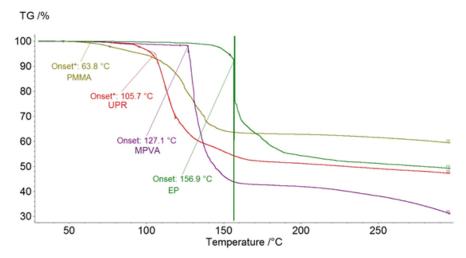


Figure 1. TG data of composite materials containing 50 wt.% of EFA.

terials show much worse results: (40 ± 5) s. for UPR, more than (100 ± 5) s. for PMMA. Thus, using EP as a matrix for EFA is effective. EP has been selected as polymeric matrix for EFA and for production fire extinguishing composite material.

Kukdo Chemical Co. LTD is selected as the base supplier of epoxy and hardeners. It is a global manufacturer of a wide range of reagent. It catalogs includes more than 40 types of epoxy resins and more than 80 types of hardeners. In the present paper, various types of epoxy resins and hardeners are analyzed to select a polymer matrix with optimal properties.

Resins based on bisphenol-A with low (YD-115, YD-114, YD-115E) and medium viscosity (YD-127, YD-128) are used. Resins with high viscosity and solid is not considered, because they sharply limit the filling of the polymer matrix. In addition,

modified types of EP are used, such as novolac (YDPN-638) and acrylate (KDU-651). The experimental results show that the epoxy resin based on bisphenol-A types YD-115 is the most optimal for our task.

A more difficult task is the selection of hardener for epoxy. Hardener has been selected based on the following parameters: hardener should work at room temperature;

hardener exothermic peak should not exceed 90 $^{\circ}$ C; hardener viscosity no more than 3000 cPs at 25 $^{\circ}$ C; hardener is chemically inert to the shell of the EFA.

A number of hardeners are selected from the supplier. It technical data are given in Table 3.

Analysis of the results show that the KH-819 is the most optimal hardener for our task.

Hardner	Types	Viscosity at 25 ℃	Curing Condition	Disadvantages
G-640	High-imidazoline polyamide	8,000-12,000	80 °C × 2 h	Hight viscosity
G-A0432	Polyamidoamine	200-600	7 days 25 ℃	Bad curing
GX-533	Polyamidoamine/epoxy adduct	800-2,000	7 days 25 ℃	Interaction with microcapsules
KH-819	Cycloaliphatic amine	50-150	7 days 25 ℃	-
KH-835	Cycloaliphatic amine	20-40	Gel time 50 min	Hight exothermic temperature
KH-500	Polyamine modified	500-4,000	Gel time 12 min	Hight exothermic temperature
TETA	Aliphatic amines	500-1000	7 days 25 ℃	Interaction with microcapsules

Table 3. Types of Hardeners used for EP

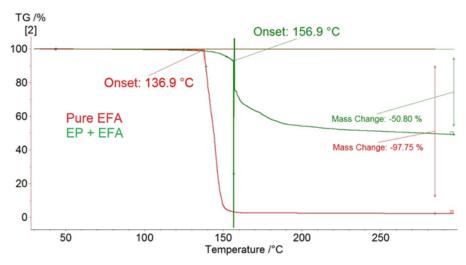


Figure 2. TG data of fire extinguishing composite materials based on EP and containing 50 wt% of EFA

3.3 The effect of EP on the kinetics and temperature of decapsulation and thermal stability of EFA

Decapsulation of EFA in a narrow time and temperature range to quickly achieve the necessary quantity of fire extinguishing agent should be ensured by the selected polymer. The effect of EP on the kinetics and temperature of decapsulation of EFA are analyzed. As mentioned above, EP increases decapsulation temperature of EFA. The Figure 2 shows a TG curve of EP containing EFA and pure EFA. Epoxy increases the decapsulation temperature from 130 °C to 155 °C. The reactive kinetics of the decapsulation of fire extinguishing composite material containing EFA explain the artifact on the TG curve. It is intense "jumping" of the sample inside the crucible.

The thermolysis data of fire extinguishing composite materials containing EFA confirm the reactive kinetics of decapsulation. Holding the samples for 10 min at 200 $^{\circ}$ C in a muffle furnace and a gas-permeable container lead to a mass loss of 45 \pm 6 wt.%. The rapid decapsulation process lead to the complete destruction of the sample of fire extinguishing

composite material containing EFA. According to the results of measurements, all volume of EFA included in the material are decapsulated. In this case, the weight loss of the sample of pure epoxy resin under similar conditions does not exceed 1 wt.%.

An important characteristic of an encapsulated fire extinguishing agent is its thermal stability over time. It is determined by the tightness of the capsule shell and subsequently determines the shelf life of the final product, as well as the processing regime of the encapsulated fire extinguishing substance when it is added to the polymer matrix. According to the method described above, a number of measurements were carried out under isothermal conditions. In all cases, the thermogravimetric curve is a monotonic dependence. Data on mass changes depending on the exposure temperature are given in the Table 3. We note that it is not possible to compare these characteristics with the results of the authors (8), since the authors conducted an exposure in time only at room temperature. For a composite material containing 50% EPA by weight, the calculation is carried out with adjustment for its content in the matrix.

Tab	le 4.	Results	of	the	Thermal	Stability	Measurements
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Exposure Temperature, °C	Mass Ch	nange, %
	Pure EFA	EFA @ EP Matrix
60	2.2	0.3
80	3.5	0.4
100	8.1	2.1

Table 5. Results of the Pull-off Adhesion Test

Base-mold Material	Pull-off Force
Stainless Steel	21 MPa
Aluminum	23 MPa
Borate Glass	15 MPa
UHMV PE	10 MPa
RTV (Additive) Silicon Rubber	< 0.1 MPa
HTV Silicone Rubber	1.4 MPa
HTV Silicon Rubber + Siloxane Fluid	< 0.1 MPa

As can be seen from the Table 4, the polymer matrix of the epoxy resin has a strong positive effect on the stability of EFA at all exposure temperatures. Weight loss decreases 7.3 times (at 60 $^{\circ}$ C), 8.6 (at 80 $^{\circ}$ C) and 3.9 times (at 100 $^{\circ}$ C). We attribute this fact to the high affinity of the materials of the EFA shell and the polymer matrix, due to which the permeability of the system for the EFA core material sharply decreases. In addition, the EFA shell has a certain porosity, which, apparently, is greatly reduced due to the penetration into the open pores of a flowing uncured epoxy resin. If the last statement is true, then using matrix with high viscosity and high curing speed, the positive effect on thermal stability will not be so high. Thus, good thermal stability values are achieved for EFA and EFA in an epoxy matrix at temperatures well above the boiling point of a pure fire extinguishing agent (49.2 °C).

3.4 Choice of base/mold materials

The method of casting the reaction medium (a mixture of epoxy resin, hardener and EFA) is used for the manufacture of sheet-shaped samples. In this context, the choice of base/mold material is an important task. The cured epoxy resin should have the least adhesion to the selected substrate material to allow free release of the cured sample. It is the basic requirement for choosing a form.

Among the materials are selected: stainless steel, aluminum, borate glass, ultra-high molecular weight polyethylene (UHMV PE), silicone additive curing rubber, high temperature vulcanization silicone rubber, high temperature vulcanization

silicone rubber doped with siloxane fluid.

Based on the results of pull-off tests, the following forces are determined (Table 5).

Thus, the best test results showed additive curing silicone (< 0.1 MPa) and high temperature vulcanization silicone doped with siloxane fluid (< 0.1 MPa) in an amount of 5 wt% The cured composite material showed significantly greater adhesion to a siloxane-free HTV silicone (1.4 MPa). The fundamental difference between RTV rubber and HTV rubber is the presence of terminal hydroxyl groups. This explains the different adhesive ability of the composite material. The addition of siloxane fluid reduced the pull-out force, but this effect was short-lived. The reason is that the siloxane liquid did not participate in vulcanization, it accumulated in the pores and over time its emission to the surface of the base/ mold. As a result of this, a "layer" was formed between the cured sample and the base/mold, which reduces adhesion. After the manufacture of several samples, the emission decreased and the pull-off force approached the standard value of 1.4 MPa.

According to the results of measurements, it can be concluded that the best material for molding is additive curing silicone rubber without terminal hydroxyl groups.

3.5 Thermomechanical properties

Figure 3 shows the results of dilatometric analysis of a sample of the composition YD-115 - KH-819 and YD-115 - KH-819 - EFA. The plots are the temperature dependences of elongation (Solid lines) and CTE (Dash lines). As you can see

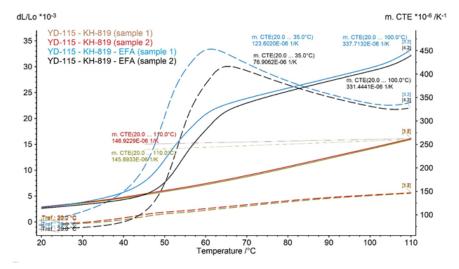


Figure 3. Temperature dependence of elongation and CTE of samples.

the graph corresponding to the cured epoxy resin without filling is a monotonous dependence. This indicates the absence of phase transitions of the first-order and second-order (In particular glass transition) in this temperature range. The average CTE in the range of 20 $^{\circ}$ C-110 $^{\circ}$ C was 146.4 \times 10⁻⁶ 1/K.

A filled epoxy resin, has a characteristic step located in the temperature range 46 $^{\circ}$ C-60 $^{\circ}$ C. In this case, a sharp increase in the relative elongation (Fourfold increase) is observed, and the CTE in the peak reaches $400\text{-}450 \times 10^6$ 1/K. The average CTE in the range of 20 $^{\circ}$ C-110 $^{\circ}$ C was 334×10^6 1/K, which is 2, 3 times higher than the corresponding value for the unfilled composition. This phenomenon is not a transition of glass transition, since after the completion of a stepwise change in the graph, a monotonic increase in linear dimensions is observed.

As already noted, the matrix does not have phase transitions in a given temperature range. Therefore, the anomalous behavior of the composite material is caused by the presence of EFA. The reason for the sharp increase in CTRLR at 46 $^{\circ}$ C-60 $^{\circ}$ C is most likely due to the relative change in the diameter of the EFA's capsule. This is supported by the correlation of the onset of a stepwise change in the thermomechanical characteristics and the boiling point of perfluoro(2-methyl-3-pentanone) (49.2 $^{\circ}$ C).

3.6 Climate tests of fire extinguishing composite material containing EFA

The polymer matrix must retain the properties of EFA during long-term storage⁽¹⁷⁾. It must protect EFA from high humidity, high temperature (In the range from a temperature above the boiling of a liquid fire extinguishing agent to the decapsulation temperature of EFA), ultraviolet radiation. In the work, climate tests were carried out to study the protective

properties of EP polymer matrix.

The properties of EFA and EP composite material containing EFA under the influence of high humidity or high humidity and temperature from 25 $^{\circ}$ C to 60 $^{\circ}$ C are analyzed. For this experiment, the samples of pure EFA (Sample 1-2) and samples of EP composite containing EFA (Sample 3-8) were kept at a relative humidity of 80% for 96 hours. The influence of high humidity or high humidity and temperature on the fire extinguishing time and mass lost is analyzed. The values of fire extinguishing time are determined in accordance with 2.3.4, values of mass lost are determined using analytical weights. Table 6 shows that high humidity strongly affects EFA and slightly affects the properties of EP composite containing EFA. The mass loss of EFA at 60 $^{\circ}$ C is 15%, the mass loss of EP composite containing EFA under the same conditions is only 0.4%. The mass loss for all EFA@EP matrix changes slightly. The average time of fire extinguishing of composite increases from 19 to 24 s compared to a sample 3 not exposed to humidity.

The effect of UV radiation on the properties of EFA and EP composite material containing EFA are analyzed. It is known⁽¹³⁾ that NovecTM1230 decomposes under the influence of UV. Samples of pure EFA and EP composite containing EFA were kept at the average UV radiation value (5000 MJ/m²) from 1 to 50 hours at 25 °C. After that the fire extinguishing time and mass lost were analyzed. The results in Table 5 are shown that UV affects EFA. Sample 2 loses 6% of mass in 50 hours. At the same condition the mass lost of EFA@EP matrix is 0.8% and UV not affect the fire extinguishing time. Epoxy matrix protects EFA from UV.

The results presented in Tables 6 and 7 are shown that the EP polymer matrix protects the EFA from high humidity, high

No.	Sample	Condition	Temperature, ℃	Fire Extinguishing, s	Mass Lost, %
1	pure EFA	Humidity 80%	25	-	6
2	pure EFA	Humidity 80%	60	-	15
3	EFA@EP matrix	Without humidity	-	19±2	-
4	EFA@EP matrix	Humidity 80%	25	19±2	0.2
5	EFA@EP matrix	Humidity 80%	35	22±2	0.3
6	EFA@EP matrix	Humidity 80%	45	20±1	0.3
7	EFA@EP matrix	Humidity 80%	55	22±2	0.4
8	EFA@EP matrix	Humidity 80%	60	24±1	0.4

Table 6. Result of Climate Tests of EP Containing EFA

Table 7. Result of UV Tests

No.	Sample	Condition	Fire Extinguishing, s	Mass Lost, %
1	pure EFA	1 hour, 5000 MJ/m ²	-	1
2	pure EFA	50 hour, 5000 MJ/m ²	-	8
3	EFA@EP matrix	without UV	21 ± 2	0.2
4	EFA@EP matrix	1 hour, 5000 MJ/m ²	21 ± 2	0.2
5	EFA@EP matrix	5 hour, 5000 MJ/m ²	22 ± 2	0.3
6	EFA@EP matrix	10 hour, 5000 MJ/m ²	22 ± 2	0.5
7	EFA@EP matrix	36 hour, 5000 MJ/m ²	24 ± 2	0.7
8	EFA@EP matrix	50 hour, 5000 MJ/m ²	23 ± 1	0.8

humidity and temperature from up to 60 °C and UV radiation.

4. Conclusions

The positive effect of epoxy resin on the kinetics of decapsulation, temperature of decapsulation and storage stability of EFA has been established. EP increases the decapsulation temperature from 130 °C to 155 °C. The high affinity of the epoxy resin to EFA shell can be explained. TG and thermolysis data show that EFA in EP decapsulated reactively in a narrow temperature range. Fire extinguishing composite material containing EFA loses of 45 \pm 6 wt.% for 10 min at 200 °C. It is means that all EFA included in the EP decapsulated. The results of isothermal thermogravimetric analysis clearly show that epoxy matrix increases thermal stability (A tendency to leak) of the EFA more than 3.9 times (In comparison with the pure EFA).

The protective effect of EP on the storage stability (High humidity, high humidity and temperature from 25 $^{\circ}$ C to 60 $^{\circ}$ C, UV radiation) of EFA has been found. The mass loss of EFA at 60 $^{\circ}$ C and 80% humidity is 15%, the mass loss of EP composite containing EFA under the same conditions is only 0.4%. The mass loss of EFA under UV radiation value (5000 MJ/m²) for 50 hours is 6%. At the same condition the mass

lost of EP composite containing EFA is 0.8%. Moreover, UV and high humidity do not affect the fire extinguishing time of EP composite containing EFA. Fire extinguishing composite material containing EFA can be used in appropriate conditions.

There is a sharp change in CTE (at a peak of 400-450 \times 10⁻⁶ 1/K) in the composite material in the range 42 $^{\circ}$ C-60 $^{\circ}$ C. This behavior is due to the phase transition of the material of the EPA core.

The different types of polymer matrix to create a fire extinguishing composite material containing EFA are analyzed in the present paper. It is found that only epoxy resin increases the temperature of decapsulation of EFA among the selected polymers (MPVA, UPR, PMMA and EP). For the manufacture of sheet-shaped samples the method of casting the reaction medium (A mixture of epoxy resin, hardener and EFA) is used. Based on the results of pull-off tests, the best test results showed additive curing silicone (< 0.1 MPa). High temperature vulcanization silicone doped with siloxane fluid (< 0.1 MPa) in an amount of 5 wt.% showed good results too. After the manufacture of several samples, the emission of siloxane fluid decreases and the pull-off force approaches the standard value of 1.4 MPa.

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References

- A. Bahadori, "Safety and Firefighting Equipment, Part 1. Personnel Protection and Safety Equipment for the Oil and Gas Industries", pp. 355-431 (2015).
- 2. D. Linden Reddy, "Linden's Handbook of Batteries", Forth ed., McGraw Hill (2011).
- D. Rosewater and A. Williams, "Analyzing System Safety in Lithium-ion Grid Energy Storage", Journal of Power Sources, Vol. 300, pp. 460-471 (2015).
- Q. Wang, B. Mao, S. I. Stoliarov and J. Sun, "A Review of Lithium Ion Battery Failure Mechanisms and Fire Prevention Strategies", Progress in Energy and Combustion Science, Vol. 73, pp. 95-131 (2019).
- P. Ribiere, S. Grugeon, M. Morcrette, S. Boyanov, S. Laruellea and G. Marlair, "Investigation on the Fire-induces Hazards of Li-ion Battery Cells by Fire Calorimetry", Energy & Environmental Science, Vol. 5, pp. 5271-5280 (2012).
- J. Warner, "Battery Management System Controls. The Handbook of Lithium-Ion Battery Pack Design", pp. 91-101 (2015).
- L. H. Saw, H. M. Poon, H. S. Thiam, Z. Cai, W. T. Chong, N. A. Pambudi and Y. J. King, "Novel Thermal Management System using Mist Cooling for Lithium-ion Battery Packs", Applied Energy, Vol. 223, pp. 146-158 (2018).
- W. Wu, S. Wang, W. Wu, K. Chen, S. Hong and Y. Lai, "A Critical Review of Battery Thermal Performance and Liquid Based Battery Thermal Management", Energy Conversion and Management, Vol. 182, pp. 262-281 (2019).
- A. A. Sertsova, S. I. Marakulin and E. V. Yurtov, "Metal Compound Nanoparticles: Flame Retardants for Polymer Composites", Russian Journal of General Chemistry, Vol. 87, No. 6, pp. 1395-1402 (2017).

- Z. An, L. Jia, X. Li and Y. Ding, "Experimental Investigation on Lithium-ion Battery Thermal Management Based on Flow Boiling in Mini-channel", Applied Thermal Engineering, Vol. 117, pp. 534-543 (2017).
- J. L. Pagliaroa and G. T. Linteris, "Hydrocarbon Flame Inhibition by C6F12O (Novec 1230): Unstretched Burning Velocity Measurements and Predictions", Fire Safety Journal, Vol. 87, pp. 10-17 (2017).
- N. Taniguchi, T. J. Wallington, M. D. Hurley, A. G. Guschin, L. T. Molina and M. J. Molina, "Atmospheric Chemistry of C2F5(O)CF(CF3)2: Photolysis and Reaction with Cl Atoms, OH Radicals and Ozone", The Journal of Physical Chemistry A, Vol. 119, pp. 2674-2679 (2003).
- D. A. Jackson, C. J. Young, M. D. Hurley, T. J. Wallington and S. A. Mabury, "Atmospheric Degradation of Perfluoro-2-methyl-3-pentanone: Photolysis, Hydrolysis and Hydration", Environmental Science & Technology, Vol. 45, pp. 8030-8036 (2011).
- 14. A. D. Vilesov, N. N. Saprykina, R. V. Stepanova, O. M. Suvorova, M. S. Bosenko, M. S. Vilesova and R. P. Stankevichb, "Microencapsulated Fire-extinguishing Fluids and Reactive Fire-extinguishing Composites Formed on Their Basis1", Polymer Science. Series A,. Vol. 54, No. 6, pp. 499-504 (2012).
- G. X. Wang, W. B. Xu, Q. Hou and S. W. Guo, "Microwave-assisted Synthesis of Poly (urea-formaldehyde)/ Lauryl Alcohol Phase Change Energy Storage Microcapsules", Polymer Science - Series B, Vol. 58, pp. 321-328 (2016).
- G. Wang, W. Xu, Q. Hou and S. Guo, "A Simple Sonochemical Method for Fabricating Poly (Methyl Methacrylate)/Stearic Acid Phase Change Energy Storage Nanocapsules", Ultrasonics Sonochemistry, Vol. 27, pp. 403-407 (2015).
- A. D. Vilesov, O. M. Suvorova, V. E. Yudin, N. N. Saprykina, M. S. Vilesova and R. P. Stankevich, "Novel Microencapsulated Liquid Fire Extinguishers with a Nanomodified Microcapsule Shell", Polymer Science - Series B, Vol. 56, pp. 512-519 (2014).