PROBLEMS AND PROSPECTS OF FIRE PREVENTION AND EXTINGUISHING

Scientific article UDC 622.276; DOI: 10.61260/2304-0130-2024-4-49-58 THE USE OF THERMALLY CONDUCTIVE POLYIMIDE FOILS FOR THE PROTECTION OF MULTIPOINT FIRE DETECTORS

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Abstract. The requirements for protective materials capable of reducing the likelihood of false fire alarms due to external mechanical and electromagnetic influences while maintaining the basic tactical and technical characteristics are formulated. The strategies for creating self-healing polymer thermally conductive composites are analyzed. The results of a study of the mechanical properties of polyimide foils under tension are shown, as well as graphs of the effectiveness of the process of self-healing of the thermally conductive properties of polymers based on oxyethyl ether and polydimethylsiloxane reinforced with graphene in the direction along and across the polymer matrix after 10 cycles of mechanical action. It is concluded that such a foil can be used as a promising protective material for the installation of multipoint fire detectors.

Key words: multipoint fire detectors, polyimide foil, graphene, polymer matrix

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Introduction

Fire detectors are part of any fire alarm system and are technical means that transmit a notification to a reception and control device.

Fire safety of modern industrial facilities is facilitated by the availability of fire alarm systems, which widely use linear and multipoint thermal fire detectors. Such systems make it possible to detect signs of fire at an early stage of its occurrence in large industrial area, which may also have a complex configuration [1, 2]. The efficiency of multipoint fire detectors (MFD) is close to the efficiency of linear ones, however, the design of the corresponding sensing elements (SE) allows them to be placed in hard-to-reach locations of industrial premises, which expands their scope of use compared to linear fire detectors [3].

The appearance of the thermal sensor used in multipoint systems is shown in fig. 1.



Fig. 1. Appearance of the SE heat detector protected by polyimide foils

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To form a multipoint system, individual SE's are connected by special communication lines, the so-called «cable tails» (fig. 2), which also need protection.



Fig. 2. Connection of MFD components

High resistance to electromagnetic and mechanical influences is required from fire detectors. Technological interference should not cause false alarms of these devices. There are also problems related to contamination of the external surface of the detectors [4].

That is why there is a need to search for new protective materials that can reduce the likelihood of false alarms due to external mechanical and electromagnetic influences, while maintaining the basic tactical and technical characteristics. Such materials must:

- have the necessary durability characteristics that allow them to be used repeatedly both for mounting MFD cables and for their mechanical protection;

- maintain necessary thermal conduction, which does not worsen SE MFD performance;

- have electrically conductive properties that make it possible to use such a material to shield MFD cables from the external electromagnetic effects of industrial facility equipment [5].

Polyimide foils with the necessary mechanical strength, high thermal and electrical conductive properties can become such materials, and if they have the ability to self-heal possible damage, the MFD service life can be extended [6].

An effective strategy for creating self-healing polymer thermally conductive composites is the introduction of a self-healing polymer matrix into the fillers. Optimization of molecular crosslinking and dynamic reversible supermolecular interaction (π - π folding, H-bonds and metal ligand) is considered a promising direction in improving the technology of creating self-healing polymers.

The organization of H-bonds, in addition to reversible interactions with strong cross-links, seems to be an effective technology for creating new polymers with high strength and the ability to rapidly self-heal. In this sense, graphene has high strength, thermal conductivity, and electrical conductivity, and graphene-based fillers are widely used to reinforce polymers in the production of functional composites. In [9], a polymer based on oxyethyl ether and polydimethylsiloxane, blocked by a vinyl end as a matrix, and a graphene foil as a conductive layer or framework under high discharge was proposed.

Thus, the task arises in assessing the stability of maintaining the mechanical and heatconducting properties of polyimide foils during installation and subsequent operation of multipoint fire detectors.

Research methods

In the process of polymer synthesis to a mixture of oxyethyl ether and polydimethylsiloxane in various molar ratios (1:1, 1:2, 1:3, 3:1 and 2:1) 20 ml of dimethylacetamide were added, followed by stirring at a temperature of 25 °C for 2 hours. Then 0,1 mmol 16,41 mg of 2-methylpropionitrile

was added and the reaction was maintained at a temperature of 67 °C for a day in an argon medium. The reaction product was precipitated in deionized water, and the white precipitate was dissolved in ethyl acetate. The resulting solution was poured into a polytetrafluoroethylene mold, dried at a standard temperature of 25 °C for 12 hours, and then dried at 60 °C for a day to obtain a sample [10].

The graphene foil was attached to a 0,3 mm thick heat shrinkable sheet that contained glue on one side, and the sheet was shrunk by uniformly heating from the edges using a heat gun at 150 °C (shrinkage ratio 1:5). The material was then immersed in anhydrous ethanol for 12 hours. The material was separated from the matrix to obtain a foil, which was soaked in a mixture of oxyethyl ether, polydimethylsiloxane and ethyl acetate, dried at 25 °C for 12 hours, and then dried in vacuum for 24 hours. This process was repeated until the graphene foil completely covered the outer surface of the composite [11].

The mechanical properties of polyimide films reinforced with graphite fillers were investigated using the electron XQ-46D universal testing machine. The sample sizes were $35,0=12,8=0,25 \text{ mm}^3$, and the stretching rate was 5 mm/min. The samples were loaded (compression 0=50 %), unloaded and reloaded 100 times.

The electrical characteristics of the samples were studied using the LCR TH2830 measuring system. The coefficients of thermal conductivity and thermal conductivity of cylindrical samples (diameter 10 mm, thickness 3 mm) were measured at the Xiangtan Xiangke DRL-2A installation.

The results of the study and their discussion

Fig. 3 shows the results of a study of the mechanical properties of polyimide foils under tension (the ratio of oxyethyl ether and polydimethylsiloxane x = 1:0, 3:1, 2:1, 1:1, 1:2, 2:3, 1:3 and a temperature of 25 °C).



Fig. 3. Strength (P) and elongation (U) of polyimide films at different proportions of oxyethyl ether and polydimethylsiloxane

The polyimide film showed a sufficiently high tensile strength $(0,06 \pm 0,01 \text{ MPa})$ and elongation (1,800 %), however, the tensile strength of the non-reinforced foil was lower than that of reinforced polyimide films at molar ratios of oxyethyl ether and polydimethylsiloxane $x = 1:2, 2:3 \mu 1:3$.

The relative elongation of the non-reinforced polyimide film turned out to be greater than that of the reinforced films (x = 1:0, 3:1, 2:1). These results showed that reinforcing the polymer structure with graphene filler increases its strength compared to the strength achieved by forming a polyimide foil structure based on H-bonds.

The non-reinforced polyimide film showed increasing self-healing efficiency as the temperature increased. The recovery efficiency was the same at room temperature and 40 $^{\circ}$ C (fig. 4).



Fig. 4. Self-healing efficiency of non-reinforced polyimide film

The experiment showed that the optimal condition for rapid self-healing of an unreinforced polyimide film is its heating at a temperature of 25 °C for 10 minutes.

For elastomers based on reinforced polyimide composites, their mechanical characteristics deteriorated after irreversible damage or destruction during bending or concentration of interfacial stresses under real operating conditions of multipoint fire detectors. The self-healing properties of composites are also influenced by the chemical activity and movement of chains of polymer segments [11]. Compared to the self-healing of electro- and thermally conductive properties, self-healing of the mechanical characteristics of reinforced polyimide composites is a more complex process.

The relative elongation of the graphene foil itself was 320 %, and the tensile strength and elongation of reinforced polyimide composites were $2,23 \pm 0,15$ MPa and 270 %, respectively.

The width and thickness of the reinforced polyamide composite sample were 10,0 and 3 mm, respectively. Fig. 5 shows the dependence of the tensile strength of the test sample with or without unilateral incision damage (1,0 mm incision width) – tested at a rate of 5 mm/min.



Fig. 5. Graphical stress versus strain dependences for undamaged and damaged samples

To quantify the self-healing ability of reinforced polyimide composites, the sheet was cut into two parts and kept at a standard temperature of 25 °C for 0,2 hours. As shown in fig. 6, the tensile strength of such a film recovered to $0,75 \pm 0,1$ MPa, and the stress was 34,09 % after self-healing for 10 minutes. The film, which relaxed for an hour, could stretch by more than 170 % and showed a tensile strength of $1,5 \pm 0,2$ MPa with a relative deformation of 68,18 %.

When the self-healing time was 2 hours, the damage repairing efficiency on the reinforced polyimide composites' surface of was similar to that in the initial state, and the mechanical properties of the material were effectively repaired.



Fig. 6. Stress-strain dependences for different relaxation duration at a temperature of 25 °C

Moreover, the relative strain values for reinforced polyimide composites were $30,5 \pm 1,50$ %, $56,81 \pm 2,2$ %, $79,52 \pm 2,50$ % and 100 % at healing temperatures of 0, 10, 20 and 25 °C, respectively (fig. 7).



Fig. 7. Stress-strain dependences for different temperatures with a relaxation duration of 2 hours

The main factors affecting the thermally conductive properties of graphene-reinforced polymers based on oxyethyl ether and polydimethylsiloxane include, first of all, density and the presence of interfacial thermal resistance. As for density, graphene materials have significant gaps at low densities, which increases their thermal resistance. As these gaps are filled with polymer, the density of the resulting composite increases, which leads to a higher thermal conductivity of the synthesized material.



Fig. 8. Thermal conductivity coefficient of the L-reinforced polyimide foil along the polymer matrix

To test the effect of self-healing of the reinforced polyimide film structure on the self-healing of its heat-conducting properties, the thermal conductivity of the samples after mechanical action on them was investigated (fig. 8).

If the ratio between oxyethyl ether and polydimethylsiloxane is 1:1, graphene reinforcement of the polymer promotes strong adhesion occurring on the interface of the composite, which can significantly reduce its thermal resistance.

Fig. 9 illustrates the effectiveness of the process of self-healing of thermally conductive properties of graphene-reinforced polymers based on oxyethyl ether and polydimethylsiloxane along the polymer matrix after 10 cycles of mechanical action.



Fig. 9. Self-healing of thermally conductive properties of polymers at the ends of samples after mechanical action along the polymer matrix

As the ratio between oxyethyl ether and polydimethylsiloxane increased, the thermal conductivity of the material first increased and then decreased. When the ratio of oxyethyl ether and polydimethylsiloxane was 1:1, the initial thermal conductivity of the composite was the highest, and the self-healing efficiency of its heat-conducting properties after the first and tenth cycles of mechanical action was 98,65 % and 97,83 %, respectively.

The measurements confirmed the anisotropy of the thermally conductive properties of graphene-reinforced polymers based on oxyethyl ether and polydimethylsiloxane. The results of the investigation of the heat-conducting properties of the samples in the direction of heat propagation across the polymer matrix are shown in fig. 10, 11.



Fig. 10. Coefficient of thermal conductivity of reinforced polyimide film across polymer matrix

The thermally conductive properties along and across the polymer matrix showed the same tendency depending on the ratio of oxyethyl ether and polydimethylsiloxane: when it was 1:1, the thermally conductive properties were maximal. For the direction across the polymer matrix, the initial thermal conductivity was $8,3 \pm 0,2$ W/(m*K), and the self-healing efficiency of thermal conductivity reached 100 % after 10 cycles (fig. 11).



Fig. 11. Self-healing of the thermally conductive properties of polymers on the lateral surface of the samples after mechanical action across the polymer matrix

The electrical conductivity of a polymer based on oxyethyl ether and polydimethylsiloxane reinforced with graphene was measured during mechanical action on the sample. Fig. 12 shows a diagram of such an experiment.



Fig. 12. Installation for measuring the electrical conductivity of a sample during mechanical action on it

The results of measuring the electrical resistance of polymer samples based on oxyethyl ether and polydimethylsiloxane, non-reinforced and graphene-reinforced, are shown in fig. 13.



Fig. 13. Electrical resistance of polyimide foil under deformation conditions

The sizes of the studied samples were $35,0\times10,0\times0,25$ mm³. The average value of the electrical resistance of the reinforced sample in the state of tension was $0,865 \pm 0,005$ Om, which corresponds to the resistivity 61,8 Om·mm²/m and commensurate with the resistivity of carbon brushes (40 Om·mm²/m).

Conclusion

1. A polymer foil based on oxyethyl ether and polydimethylsiloxane reinforced with graphene has a high tensile strength $(0,06 \pm 0,01 \text{ MPa})$, which persists under repeated mechanical stress and even minor mechanical damage (incision width up to 1 mm). This allows to consider the polymer under study as a promising protective material for the installation of multipoint fire detectors at industrial facilities.

2. The value of the thermal conductivity coefficient of the polymer foil under study along and across the polymer matrix was $13 \pm 0.2 \text{ M} 8.3 \pm 0.2 \text{ W/(m·K)}$ accordingly, this is commensurate with the thermal conductivity of some metal alloys and significantly exceeds the heat-conducting properties of traditional materials used for protection of MFD SE.

3. Although the electrical resistivity of a polymer based on oxyethyl ether and graphenereinforced polydimethylsiloxane ($61.8 \text{ Om} \cdot \text{mm}^2/\text{m}$), significantly less than that for traditional polymer materials, the effectiveness of protecting fire alarm communication lines from electromagnetic interference with such a polymer film needs additional study.

Fire alarm systems that use linear and multipoint thermal fire detectors make it possible to detect signs of fire at an early stage of its occurrence in industrial premises of large area and complex configuration. Despite the fact that the efficiency of multipoint fire detectors is close to the efficiency of linear ones, the design of the corresponding sensitive elements of multipoint fire detectors allows them to be placed in hard-to-reach locations of industrial premises, which expands the scope of use of multipoint fire detectors compared to linear ones.

List of sources

1. Analysis of the effectiveness of thermal multipoint fire detectors / V.L. Zdor [et al.] // Fire and explosion safety. 2004. Vol. 13. N_{2} 1. P. 30–32.

2. Modern fire early detection systems / M.V. Savin [et al.] // Fire and explosion safety. 2003. Vol. 12. № 6. P. 70–73.

3. Calculation of parameters of multipoint fire detectors of summing type during design / G.M. Karnaukhov [et al.] // Fire safety. 2005. № 1. P. 106–112.

4. Gong Ha Song, Kang Kwang Soo, Yang Jung Song. Comparative study of conventional and analog fire sensors with different numbers of fire detectors // International journal of control and automation. 2018. № 3. Vol. 9. P. 299–308.

5. Sapronov S.V. Automated control of the security alarm system / Product quality: control, management, improvement, planning: collection of scientific articles of the 4th Intern. youth scien. and pract. conf.: 3 Vol. 2017. P. 283–286.

6. Superior toughness and fast self-healing at room temperature engineered by transparent elastomers / S.M. Kim [et al.] // Adv. Mater. 2018. № 30 (1). P. 1705145. DOI: 10.1002/adma. 201705145.

7. Self-healing thermally conductive adhesives / U. Lafont [et al.] // J. Intell. Mater. Syst. Struct. 2014. № 25 (1). P. 67–74. DOI: 10.1177/10453 89X13498314.

8. A self-healing silicone/BN composite with efficient healing property and improved thermal conductivities / L. Zhao [et al.] // Compos. Sci. Technol. 2020. № 186. P. 107919. DOI: 10. 1016/j.comps citech. 2019.

9. Lightweight, flexible cellulose-derived carbon aerogel@reduced graphene oxide/PDMS composites with outstanding EMI shielding performances and excellent thermal conductivities / P. Song [et al.] // Nano-Micro Lett. 2021. № 13. P. 91. DOI: 10.1007/s40820-021-00624-4.

10. Self-healing and shape-memory properties of polymeric materials cross-linked by hydrogen bonding and metal-ligand interactions / Yu. Kobayashi [et al.] // Polym. Chem. 2019. № 10 (33). P. 4519–4523. DOI: 10.1039/C9PY0 0450E.

11. Self-healing high strength and thermal conductivity of 3D graphene/PDMS composites by the optimization of multiple molecular interactions / H. Yu [et al.] // Macromolecules. 2020. № 53 (16). P. 7161–7170. DOI: 10.1021/acs.macro mol.9b02544.

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