The use of cenospheres for the production of spheroplastics with high dielectric characteristics, obtained from ash of thermal power plant operating on solid fuel

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Abstract. Current work investigates problems of smoke emissions utilization from thermal power plants operation on solid fuel. During the work of this TPP type, a significant amount of ash is formed. During flotation, a pop-up fraction consisting of hollow spherical particles – cenosphere is distinguished from it. One of the promising applications of the cenospheres is their use as a filler in the production of spheroplastics. Cenospheres ecological safety was studied for the presence of heavy metals and the impact of water hoods on bioorganisms. Cenospheres’ shell chemical composition was determined using an X-ray fluorescence spectrometer «Спектроскан». It is determined that the cenosphere consists mainly of aluminium oxide and silicon oxide, and heavy metals are presented in trace amounts. Microorganisms’ test reactions of the daphnia magna showed the absence of toxic characteristics in the cenospheres. Considering tests results, it was concluded that use of the cenospheres in spheroplast was safe. Based on the unique composition of cenosphere shell made of aluminum and silicon oxides, it was concluded that they should be used as dielectric materials. Dielectric characteristics of spheroplastics on the basis of cenosphere and connector, polymethylphenylsiloxane resin of domestic manufacture, in the field of centimeter microwave radio range are studied by the waveguide method. The research results showed that the dielectric characteristics of spheroplastics are at a very high level. The use of polymethylphenylsiloxane connector allows not only to increase the dielectric characteristics and durability of spheroplastics, but also partially reduce the combustibility and flammability of structures.

1. Introduction
At the present time, most countries using solid-fuel thermal and electric power generation plants face the problem of the subsequent disposal of ash, a non-burned product of coal particles. The most widely used technologies are injecting ash into concrete [1-5]. However, there is no significant effect with such disposal technologies. Therefore, a more interesting option is to additionally isolate the fraction emerging in hydrocarbons, which is hollow microspheres with a continuous shell of a durable ceramic-like material [6-8]. The resulting microspheres, called the cenosphere, can be used in the production of spheroplastics. Spheroplastics are composite materials where solid or hollow microspheres are bonded with a polymer connector [9-12]. Due to the presence of the gas phase, they are characterized by a lower coefficient of thermal conductivity and occupy a significant place in the development of new thermal insulation structural materials. The presence of hollow particles provides...
them with low density, low dielectric losses, increased strength, reduced coefficient of thermal
expansion [13-15].

Combination of presented characteristics makes use of spheroplastics indispensable not only as a
filler in sandwich structures, but also as independent electrical and thermal insulation products.

The choice of connector also largely determines physical, mechanical, thermal and electrical
properties of spheroplastics. Currently, much attention is paid to organosilicon connector, including
with reactive hydroxyl groups, due to their high thermal stability and environmental safety, and the
possibility of crosslinking at relatively low temperatures [16-17].

The aim of the present work is to study the possibility of utilizing cenospheres by using them in the
production of spheroplastics with high dielectric characteristics.

2. Experiments

Cenospheres were used as a filler, which are a floating fraction of thermal power plants ash operating
on the coal of the Kuzbass coal basin. They are hollow micro-spheres with a bulk density of 300-450
kg/m3, shell consists mainly of silicon oxides and aluminum. Due to the fact that chemical
composition and structure are close to mullite, cenospheres are sometimes called hollow ceramic
microspheres. The fractional analysis of the used cenospheres showed that the main component of the
filler consists of microspheres measuring 20-40 microns in size. Appearance of cenospheres is shown
in photomicrograph (figure 1).

![Photomicrograph of cenospheres.](image)

Polymethylphenylsiloxane resin TU 2228-277-05763441-99 was used as a connector, produced at
the enterprise of OAO Khimprom (Novocheboksarsk), which is a silicon organic oligomer with
hydroxyl groups, non-toxic, which differs stability of characteristics in a wide temperature range (from
-60 °C to 300 °C). Hardening of polymethylphenylsiloxane resin (PMPS) was carried out in the
presence of a triethanolamine reaction catalyst, added in the amount of 5 % of the resin mass.

Samples of spheroplastic with a connector content up to 50 % (volumetric) were obtained by
mixing a given amount of connector and catalyst, then adding a filler, molding samples at a pressure
of 0.3 MPa and subsequent hardening at a temperature of 150 °C within 2 hours.

Determination of dielectric characteristics of spheroplastic in centimeter microwave-radio-range
was carried out by waveguide method. The measuring complex consisted of a precision measuring line
P1-20, a reconfigurable generator M31102-1 on the Gann diode (8-11 GHz), a ferrite valve and a
segment of a standard section waveguide 10x23 mm. The sample was placed inside the waveguide, the
end of which was short-circuited with a silver copper plate. Based on displacement measurements of
minimum VSWR position, the VSWR value and the known propagation constant, wavelength in the
free space $\lambda_0$ or this operating frequency and the critical wavelength in the waveguide $\lambda_{cr}$ the tangent
of the loss angle $\tan\delta$ and dielectric permeability $\varepsilon$ were calculated [8]. P Calculations of dielectric
permeability $\varepsilon$, angle of dielectric losses $\tan\delta$ were done using the MathCad software.
3. Results and discussion
At the initial stage of research, chemical composition of the cenospheres shell was determined using the X-ray fluorescence spectrometer «Spektroscan». The main components are SiO$_2$-57 % and Al$_2$O$_3$-28 %. The rest are impurities of oxides of alkaline and alkaline earth oxides of metals and carbon. Presence of heavy metals, in particular copper, on the threshold of detection. Chemical composition of the shells is very close to mullite. Test analysis by the effect of a water extract of the cenospheres on daphnia magna micro-organisms showed the absence of toxicity in this component.

Hardening of the composition occurs due to reactive lateral hydroxyl groups of PMPS.

Spheroplastic properties are determined both by the nature of the connector and filler, and by the ratio of components in it. Density of filled compositions, with a sufficient degree of accuracy is calculated by the following formula [18]:

\[ \rho_t = \rho_{sph} (1 - \theta_{con}) + \rho_{con} \theta_{con} \] (1)

where \( \rho_{sph} \) - average density of microspheres and \( \rho_{con} \) - volume fraction of the connector.

In table 1 the comparative values of calculated and experimental density of spheroplastic are shown.

| Amount of cenospheres in spheroplastic, % | Density of spheroplastic, kg/m$^3$ |
|-----------------------------------------|----------------------------------|
| Calculated | Experimental |
| 60 | 580 | 524±10 |
| 40 | 720 | 706±7 |
| 20 | 860 | 852±7 |

A slight difference in the calculated and experimental density of samples is mainly due to the non-ideal sphericity of the censor.

3.1. Dielectric characteristics in the microwave radio frequency field
PMPS-based compositions and cenospheres due to low density and high physical and mechanical characteristics could be a promising material for sealing elements of structures operating in a high-frequency radio range. Spheroplastic consists of three components: air, ceramic shell and PMPS, we can conclude that the most influence on the dielectric characteristics of the last two components is the greatest.

For heterogeneous systems, there is an analytical relationship (Lichtenecker's formula), which binds the dielectric permeability of the composition to the dielectric permeability of components [19]:

\[ \ln \varepsilon_r = \theta_1 \ln \varepsilon_{r1} + \theta_2 \ln \varepsilon_{r2} \] (2)

where \( \varepsilon_{r1}, \varepsilon_{r2} \) - dielectric permeability of the 1st and 2nd components respectively; \( \theta_1, \theta_2 \) - volume shares of the 1st and 2nd components respectively.

The dielectric properties of the cenospheres with the binding PMPS should to a large extent be determined both by the nature of the connector and the filler, and by their ratio. However, compared to previously considered cenospheres with linear polyorganosloxan as a binder, it can be assumed that
their dielectric characteristics will be significantly higher. This assumption is based on the fact that the linear polymers in the highly elastic state are described by significant dielectric losses. Experimental studies of the electrical properties of cenospheres, conducted using a measuring line at 9.8 GHz, confirmed this assumption. Table 2 shows experimental and calculated values of dielectric permeability of cenospheres. Differences between calculated and experimental values are expressed to a much lesser extent than in the case of linear polyorganosloxane binder usage.

Table 2. Calculated and experimental values of dielectric permeability of cenospheres.

| Concentration of PMPS, % | Calculated values | Experimental values |
|--------------------------|-------------------|---------------------|
|                          | PMC | PMC | PMC | PMC |
| 10 | 1.21 | 1.27 |
| 15 | 1.34 | 1.36 |
| 20 | 1.43 | 1.45 |
| 25 | 1.61 | 1.63 |

With the increase of the binder content in the spheroplastic, dielectric permeability (table 2) and tangent of the dielectric loss angle (figure 2) increase to a much lesser extent than in the case of traditional linear polydimethylsiloxanes. Increase in composition losses is associated with the replacement of air in the interspherilic space by the connector.

![Figure 2](image)

**Figure 2.** Dependence of dielectric loss tangent on the binder content in spheroplastics.

However, we must take into account the fact that PMPS has a significant expressed hydrophobic ability, apparently associated with the presence of lateral hydroxyl substituents interacting with silanol groups on the glass surface. In addition, studies have shown that the dielectric characteristics of spheroplastic filled with PMC are noticeably better than spheroplastics filled with traditional hollow glass microspheres [20]. This would seem to be a contradictory fact, since the density of spheroplastic with PMC filler is noticeably higher. But in this case, we should remember that PMC contain a minimum amount of alkali and alkaline earth metal ions, which, as a rule, do not contribute to high
dielectric characteristics. It connects with an increase in the filler surface resistance, both in a moist atmosphere and in the conditions of aggressive reagents: hydrogen chloride, dioxide and sulfur trioxide, etc. In addition, PMC contain a significant amount of silica, which, as we know, is one of the best dielectrics with the lowest dielectric loss tangent [17].

One of the main indicators of protective screens operating in the microwave technology is radio transparency. The radio transparency $T$ is determined when electromagnetic radiation passes through the material at a Brewster angle, as the ratio of the power of incoming and outgoing radiation. Figure 3 shows dependence of radio transparency on the content of PMPS in spheroplastics.

![Graph](image)

**Figure 3.** Dependence of radio transparency on the content of a connector in spheroplastics.

As in the case of dielectric losses, the curve under similar conditions is ascending. The change in electrical properties of PMPS is largely influenced by the transition of the polymer from a fiberglass to a highly elastic state. In this area, dielectric permeability reaches its maximum value. In highly elastic state, the changes in dielectric characteristics are not large.

Since the coupling PMPS is characterized by a high degree of stitching and its transition to a highly elastic state is not possible, it can be assumed that with a change in temperature, dielectric characteristics will change slightly. Moreover, the use of the PMC filler due to the absence of light-moving atoms of alkali metals allows to receive spheroplastic not depending on the change of external conditions: temperature, humidity and other factors.

4. Conclusions
The research results showed that using cenospheres as fillers, it becomes possible to create spheroplastics relatively inexpensive but quite effective in the centimeter microwave range, for producing protective radiotransparent screens of stationary and mobile radar stations, radio telescopes and other similar structures. At the same time, due to utilization of the ash fraction of thermal power plants operating on solid fuel, a significant environmental effect is achieved, associated with the reduction of load of these technogenic wastes on the environment.

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