UDC 537.3

Check for updates

Condensed Matter Physics. Dielectrics

EDN <u>OEOMHP</u>

https://www.doi.org/10.33910/2687-153X-2025-6-1-17-25

Electret properties and electrical conductivity of polypropylene-polyphenylene sulfide composites

A. A. Pavlov^[2], M. A. Kovalenko², V. A. Goldade^{2,3}, M. E. Borisova¹, S. V. Zotov²

¹ Peter the Great St. Petersburg Polytechnic University,

29 Polytechnicheskaya Str., Saint Petersburg 195251, Russia

² V. A. Belyi Metal-Polymer Research Institute of National Academy of Sciences of Belarus,

32 Kirova Str., Gomel 246050, Belarus

³ Francisk Skorina Gomel State University, 102 Sovetskaya Str., Gomel 246003, Belarus

Authors

Andrey A. Pavlov, ORCID: 0000-0001-5459-7509, e-mail: pavlov.aa.hv@mail.ru

Mikhail A. Kovalenko, e-mail: <u>mikhailkovalenko1991@gmail.com</u>

Victor A. Goldade, ORCID: 0000-0001-7964-8034, e-mail: victor.goldade@gmail.com

Margarita E. Borisova, ORCID: 0000-0003-0761-6302, e-mail: vladimirl.borisov@gmail.com

Sergey V. Zotov, ORCID: 0000-0002-4480-6503, e-mail: zotov-1969@mail.ru

For citation: Pavlov, A. A., Kovalenko, M. A., Goldade, V. A., Borisova, M. E., Zotov, S. V. (2025) Electret properties and electrical conductivity of polypropylene-polyphenylene sulfide composites. *Physics of Complex Systems*, 6 (1), 17–25. <u>https://www.doi.org/10.33910/2687-153X-2025-6-1-17-25</u> EDN <u>OEOMHP</u>

Received 4 September 2024; reviewed 28 October 2024; accepted 28 October 2024.

Funding: The study had no financial support.

Copyright: © A. A. Pavlov, M. A. Kovalenko, V. A. Goldade, M. E. Borisova, S. V. Zotov (2025) Published by Herzen State Pedagogical University of Russia. Open access under <u>CC BY-NC License 4.0</u>.

Abstract. The electret properties and electrical conductivity of polypropylene-polyphenylene sulfide (PP-PPS) composites were studied. The results reveal that the effective surface charge density is higher in fibrous-porous materials (FPM) compared to film-based composites. In the electrical conductivity-temperature dependence, a characteristic up-turn is observed at a temperature of 110 °C, where the high-temperature segment of the curve corresponds to the intrinsic conductivity of the composite. The low-temperature segment can be attributed to structural defects. Additionally, two relaxation maxima are identified in the thermally stimulated depolarization (TSD) current spectra. The low-temperature peak is associated with the charge relaxation at the matrix-filler interface, a phenomenon driven by Maxwell — Wagner polarization. The high-temperature maxima are likely related to the relaxation of charges governed by the intrinsic conductivity of PP in its amorphous phase.

Keywords: polypropylene, polyphenylene sulfide, electret, electrical conductivity, composite material

Introduction

In recent years, there has been an increasing demand for polymer composites incorporating fillers of diverse types, including dielectric fillers (metal oxides, clays) (Galikhanov et al. 2024a; 2024b; Gorokhovatskij et al. 2020), nanostructured fillers (aerosil, talc, nanotubes, montmorillonite, diatomite) (Galikhanov et al. 2019; Goldade et al. 2020; 2021; Kovalenko, Goldade 2021; Kovalenko et al. 2023; Minzagirova et al. 2021), as well as polymer blends and copolymers (Aniskina et al. 2010; Castro et al. 2024; Gorokhovatskij et al. 2022; Guliakova et al. 2024). The introduction of fillers allows to adjust various material properties, including mechanical, electrical, and optical characteristics, allowing for the fabrication of composites with tailored performance attributes (Galikhanov et al. 2024b). The investigation of the electret state in polymer composites is of significant practical importance, since the electret charge influences key performance characteristics of materials, i. e., liquid permeability, friction wear resistance, and filtration efficiency (Goldade et al. 2019; Kestelman 2000; Li et al. 2021).

The objective of this study is to investigate the electret effect in composite materials composed of polypropylene and polyphenylene sulfide. A comparison is made between film-based samples and fibrous-porous samples, as the electret state in the latter significantly influences filtration efficiency (Chen et al. 2023; Kara, Molnár 2021; Zhang 2020).

Materials and methods

The reported experiments are based on polypropylene (PP) 4445S produced by Rospolymer LLC ($T_m = 160$ °C) and polyphenylene sulfide (PFS) NHU-PPS produced by ZHEJIANG NHU SPECIAL MATERIALS CO.LTD (Tm = 230 °C). To obtain the PP-PPS composite, both powdered and granular forms of polymers were used. Mechanical mixing did not yield a homogeneous distribution of the components within the mixture. Consequently, a twin-screw extrusion method was employed using a SuPlast 25/2 extruder (China).

Following extrusion, the polymer was cooled and granulated, with the resulting granules used for subsequent sample fabrication. Two distinct sample types were analyzed: 1) fibrous-porous material (FPM) produced via melt-blowing technology (Pinchuk 2012) and 2) film samples obtained by hot pressing. FPM samples, each with a diameter of 1 cm, were cut from the PP-PPS composite, with a thickness ranging between 1–1.5 mm.

The thickness of the polymer films was $150-170 \mu m$. The following sample compositions were investigated: 1) PP (without filler); 2) PP 90 wt. % + PPS 10 wt. %; 3) PP 80 wt. % + PPS 20 wt. %; 4) PP 65 wt. % + PPS 35 wt. %. The selected component ratios were based on the superior filtration efficiency of the PP-PPS composites.

Electrets formation was achieved using corona discharge at a potential of -6 kV (Fig. 1). The initial electret potential difference was adjusted by positioning a grid in the air gap between the needle and the sample. The charge process was conducted at room temperature for 1 minute. The ion transfer from the discharge region ceased when the potentials of the sample surface and the grid became equal, allowing the electret potential difference to be set.

The electret properties of the polymer composites were evaluated using two techniques: 1) measurement of the effective surface charge density (ESCD) and 2) thermally stimulated depolarization (TSD) current spectroscopy (Gorokhovatskij 1991). The polarity and magnitude of the ESCD were determined using an IPEP-1 electrostatic field parameter meter (MNIPI, Minsk, Belarus).



Fig. 1. Schematic of the sample charging process

To study the temperature stability of electrets, measurements of thermally stimulated voltage (TSV) and thermally stimulated depolarization (TSD) currents were conducted.

The temperature dependence of TSV, denoted as U(T), allows for a visual assessment of the electret state stability in the material: the lower the temperature at which a sharp decline in U is observed, the less stable the charge. The U(T) curves were obtained at a constant heating rate of 1 K/min.

Assuming that the relaxation of the near-surface homocharge occurs due to the intrinsic conductivity of the dielectric, the temperature dependence of the conductivity can be calculated using the following formula:

$$\gamma(T) = \frac{-\varepsilon\varepsilon_0\beta}{U(T)} \cdot \frac{\mathrm{d}U}{\mathrm{d}T},\tag{1}$$

where β is the heating rate, K/s, and ε is the relative permittivity of the composite material.

The relative permittivity of composite materials was calculated using the Lichtenecker's formula (Bogorodickij 1965):

$$\lg \varepsilon = \theta_1 \cdot \lg \varepsilon_1 + \theta_2 \cdot \lg \varepsilon_2, \qquad (2)$$

where ε_1 and ε_2 represent the relative permittivity of individual components, while θ_1 and θ_2 denote the volume fractions of these components. The results of these calculations are presented in Table 1.

Table 1. Relative permittivity of PP and PP-PPS

Material	РР	PP + 10% PPS	PP + 20% PPS	PP + 35% PPS
ε	2.20	2.25	2.30	2.39

The primary method for studying charge relaxation processes is the thermally stimulated depolarization (TSD) current technique. The position of the TSD current maxima is determined by the chemical composition of the material, the charging method, and the nature of the sample's contact with the electrodes. The TSD current method is also capable of detecting moisture, impurities, and material aging.

TSD currents were measured at a constant heating rate of 2 °C/min, with an insulating layer (PTFE film, 30 μ m thick) placed between the sample surface and the electrode (Fig. 2). The resistivity of the insulating layer (~10¹⁸ ohms/m) is several orders of magnitude higher than that of the PP + PPS samples. In this configuration, the direction of the TSD current corresponds to the movement of charge carriers through the volume of the composite.



Fig. 2. TSD current measuring scheme

Results and discussion

Effective surface charge density

The effective surface charge density ESCD (σ_e) is a critical property of electrets, reflecting both the magnitude of the surface charge and the extent of the charge distribution within the material. ESCD is equivalent to the potential difference of the electret U:

$$U = \int_0^L E(x) dx = E_i L = \frac{\sigma_e}{\varepsilon \varepsilon_0} = A \sigma_e, \qquad (3)$$

where L is the thickness of the electret, E_i is the average internal field of the electret, A is a constant.

The ESCD of FPM samples prior to corona discharge treatment ranges from -0.2 to $+0.7 \ \mu C/m^2$ (Fig. 3). This value represents the technological charge present in all samples and is determined by the manufacturing process. After treatment with corona discharge, a significant increase in ESCD was recorded. As the content of PPS in the composite increased from 10% to 35%, the ESCD rose to values of -3.0 and $-6.2 \ \mu C/m^2$, respectively.

The technological charge value in the film samples lies in the range from -0.12 to $-0.3 \,\mu\text{C/m}^2$ (Fig. 4). The maximum ESCD observed after corona discharge treatment in the film samples was $-2.3 \,\mu\text{C/m}^2$, which is notably lower than the corresponding values for the FPM samples.



Fig. 3. ESCD values (μ C/m²) before (blue bars) and after (red bars) charging of FPM samples. Labels 1, 2, 3, and 4 correspond to PFS contents of 0%, 10%, 20%, and 35 wt.% in the PP + PFS composition, respectively



Fig. 4. ESCD values (μ C/m²) before (blue bars) and after (red bars) charging of film samples. Labels 1, 2, 3, and 4 correspond to PFS contents of 0%, 10%, 20%, and 35 wt.% in the PP + PFS composition, respectively

The FPM structure contains numerous air inclusions (pores or inter-fiber spaces). The local electric fields within these pores can significantly exceed the intensity of the external electric field, potentially reaching levels that approach electric breakdown of air. This phenomenon leads to a sharp increase in the number of charge carriers adsorbed on the fibers, which, in turn, results in an increase in ESCD.

The subsequent results were obtained by studying the electret properties of the film samples.

Thermally stimulated voltage. Electrical conductivity

Figure 5 shows temperature dependences of the electret potential difference $U(T)/U_0$.



Fig. 5. Temperature dependences of the electret potential difference $U(T)/U_0$: PP (1), PP 90 % + PPS 10 % (2), PP 80 % + PPS 20 % (3), PP 65 % + PPS 35 % (4)

Figure 5 shows that the most stable electret state is observed in pure polypropylene (curve 1), where the electret potential difference changes only slightly as the sample is heated to 110 °C. In contrast, the U/U_0 of the composite materials decreases almost linearly as the temperature increases.

The temperature dependence of the electrical conductivity of dielectric materials is derived from formula 1 (Fig. 6).

A notable difference in the temperature dependence of the electrical conductivity is observed between pure PP (curve 1) and the PP + PPS composites. In pure PP, the electrical conductivity decreases steadily with increasing temperature. In contrast, the composites exhibit a distinct break at approximately 110 °C, which can be attributed to the ionic conductivity mechanism in dielectrics.

The ionic conductivity of dielectrics is typically governed by two distinct mechanisms, as described by (Borisova, Kojkov 1979). At low temperatures, conductivity is primarily influenced by impurities, whereas at higher temperatures the movement of the primary ions of the material becomes the dominant factor. The temperature dependence of conductivity, $\gamma(T)$, can be expressed as:

$$\gamma(T) = A_1 e^{\left(-\frac{E_1}{kT}\right)} + A_2 e^{\left(-\frac{E_2}{kT}\right)},\tag{4}$$

where A_1 and A_2 are independent coefficients, and E_1 and E_2 are activation energies associated with the two conduction mechanisms.

In Figure 6, curve 3 is approximated by two distinct segments with different slopes. The high-temperature segment of the curve represents the intrinsic conductivity of the dielectric material, while the low-temperature region exhibits a weaker slope ($E_1 < E_2$), indicating that the conductivity in this region is primarily determined by the nature and concentration of impurities (in this case, PFS).

Physics of Complex Systems, 2025, vol. 6, no. 1



Fig. 6. Temperature dependence of the electrical conductivity: PP (1), PP 90 % + PPS 10 % (2), PP 80 % + PPS 20 % (3), PP 65 % + PPS 35 % (4)

TSD current spectra

Figure 7 shows the temperature dependences of the TSD currents.

Two relaxation maxima are evident in the TSD spectra. The low-temperature maximum ($T = 75 \div 90^{\circ}$ C) is due to the relaxation process of the charge accumulated at the interface between the matrix (PP) and the filler (PPS), which exhibit different dielectric permittivity, ε , leading to Maxwell — Wagner polarization. The activation energy for the high-temperature current maxima ranges from 1.7 to 3.8 eV and increases with higher filler concentrations.

The high-temperature maximum ($T = 135 \div 145$ °C) may be associated with a relaxation process caused by the intrinsic conductivity of PP in the amorphous phase. The accumulated charge remains stable until the crystalline phase of PP melts at approximately 160 °C.

The TSD current spectra are analyzed using discrete elementary Debye maxima, each characterized by a single relaxation time (Borisova et al. 2004). In this case, the TSD current can be expressed by the formula:

$$I_{TSD} = I_m \cdot \exp\left(\frac{W_a}{kT_m} - \frac{W_a}{kT}\right) \cdot \exp\left(-\frac{W_a}{kT_m^2} \cdot \int_{T_m}^T \exp\left[\frac{W_a}{kT_m} - \frac{W_a}{kT}\right] dT\right),$$
(5)

where k is the Boltzmann constant, T_m is the temperature at which the current reaches its maximum I_m , W_a is the activation energy, τ_m is the relaxation time at the temperature of the current maxima.

An example of the experimental and calculated data for PP + 20% PPS sample is shown in Figure 8. From the obtained graphs, the activation energies for the relaxation peaks were calculated and are presented in Table 2.



Fig. 7. TSD spectra for the PP sample (red) and composites with varying PPS content: PP + 10% PPS (A), PP + 20% PPS (B), PP + 35% PPS (C)



Fig. 8. Experimental (points) and calculated (solid line) TSD current for the PP + 20% PPS sample

Sample	<i>T_m</i> , K	I_{m} , 10 ⁻¹³ A	W_{a} , eV
PP	406	1.3	1.7
DD - 100/ DDC	357	2.4	0.6
PP + 10% PPS	410	1.6	1.9
DD - 200/ DDC	348	1.0	1.3
PP + 20% PPS	415	2.8	2.6
DD - 250/ DDC	365	1.3	0.5
rr + 55% PPS	408	2.3	3.8

Table 2. Current maxima and calculated activation energy values

The activation energy for the high-temperature current maxima varies from 1.7 to 3.8 eV, with an increasing trend as the filler concentration rises.

Conclusion

The study shows that the polarization of polypropylene samples filled with polyphenylene sulfide results in the formation of an electret state. Notably, the effective surface charge density is significantly higher in fibrous-porous materials compared to film-based materials. This increase in the ESCD is likely due to the formation of strong local electric fields within the pores, which substantially enhance the number of charge carriers, thereby boosting the ESCD.

In pure PP, the electrical conductivity decreases steadily with increasing temperature, while composites exhibit a distinct change in the conductivity curve at approximately 110 °C. The high-temperature segment of the curve reflects the intrinsic conductivity of the dielectric, while low-temperature conductivity is primarily influenced by material impurities.

Two relaxation maxima are observed in the TSD current spectra. The low-temperature maximum is associated with the relaxation of the charge accumulated at the interface between the matrix (PP) and the filler (PFS), which exhibit different dielectric permittivity, ε , leading to Maxwell — Wagner polarization. The high-temperature maximum can be attributed to a relaxation process caused by the intrinsic conductivity of polypropylene in the amorphous phase.

To enhance the electret properties, further investigations are recommended on composite materials based on polypropylene with lower concentrations of polyphenylene sulfide, as the greatest influence of the filler on the electret characteristics of the composite material is observed at filler concentrations below 10% (Galikhanov et al. 2019; Gorokhovatskij et al. 2020; Kovalenko et al. 2023). However, it is important to note that the electret state of filter materials does not always correlate with improved filtration efficiency (Xiao 2015). Therefore, a careful balance must be struck between the desired material properties and the technical and economic constraints of the production process.

Conflict of Interest

The authors declare that there is no conflict of interest, either existing or potential.

Author Contributions

All the authors contributed to the final work and participated in the writing of the article.

References

Aniskina, L. B., Viktorovich, A. S., Galikhanov, M. F. et al. (2010) Polielektrolitnaya model' voloknitov na osnove polietilena i polipropilena [Polyelectrolyte model of fibrites based on polyethylene and polypropylene]. Izvestiya Rossijskogo gosudarstvennogo pedagogicheskogo universiteta im. A. I. Gertsena — Izvestia: Herzen University Journal of Humanities & Sciences, 135, 24–36. (In Russian)

Bogorodickij, N. P. (1965) *Teoriya dielektrikov. [The theory of dielectrics]*. Leningrad: Energiya Publ., 344 p. (In Russian)

Borisova, M., Kojkov, S. (1979) *Fizika dielektrikov [Physics of dielectrics]*. Leningrad: Leningrad State University Publ., 240 p. (In Russian)

- Borisova, M. E., Galukov, O. V., Tsatsynkin, P. V. (2004) *Fizika dielektricheskikh materialov. Elektroperenos i nakoplenie zaryada v dielektrikakh [Physics of dielectric materials. Charge transfer and preservation in dielectrics]*. Saint Petersburg: Saint Petersburg State University Publ., 106 p. <u>https://doi.org/10.18720/SPBPU/2/si20-477</u> (In Russian)
- Castro, R. A., Karulina, E. A., Galikhanov, M. F. et al. (2024) Relaxation of electric charge in polymer blends based on low-density polyethylene and copolymer of ethylene with vinyl acetate. *St. Petersburg State Polytechnical University Journal: Physics and Mathematics*, 17 (3), 36–45. <u>https://doi.org/10.18721/JPM.17304</u> (In English)
- Chen, C., Chen, G., Zhang, J. et al. (2023) Study on corona charging characteristic of melt-blown polypropylene electret fabrics. *Journal of Electrostatics*, 121, article 103782. <u>https://doi.org/10.1016/j.elstat.2022.103782</u> (In English)
- Galikhanov, M. F., Minzagirova, A. M., Spiridonova, R. R. (2019) Modifying the properties of polyethylene electrets through the incorporation of montmorillonite. *Surface Engineering and Applied Electrochemistry*, 55, 679–683. <u>https://doi.org/10.3103/S106837551906005X</u> (In English)
- Galikhanov, M. F., Minzagirova, A. M., Guliakova, A. A. et al. (2024a) Electret composite materials based on polyethylene and petroleum asphaltenes. *IEEE Transactions on Dielectrics and Electrical Insulation*, 31 (5), 2335–2342. <u>https://doi.org/10.1109/TDEI.2024.3434774</u> (In English)
- Galikhanov, M. F., Zhang, X., Ma, X. et al. (2024b) The effect of modifier on electret properties and hardness of epoxy composite material. *IEEE Transactions on Dielectrics and Electrical Insulation*, 31 (5), 2343–2349. <u>https://doi.org/10.1109/TDEI.2024.3452655</u> (In English)
- Goldade, V. A., Kovalenko, M. A., Garbaruk, V. Yu. et al. (2020) Formirovanie i relaksatsiya zaryada v nanokompozitakh na osnove polietilena [Formation and relaxation of charge in nanocomposites based on polyethylene]. *Vestnik Grodnenskogo gosudarstvennogo universiteta im. Yanki Kupaly. Seriya 6. Tekhnika — Vesnik of Yanka Kupala State University of Grodno. Series 6. Engineering Science*, 10 (2), 52–63. (In Russian)
- Goldade, V. A., Kovalenko, M. A, Zotov, S. V. (2021) Electret charge in nanocomposites based on polyethylene. *International Scientific Journal Theoretical & Applied Science*, 193 (11), 759–765. <u>https://dx.doi.org/10.15863/</u> <u>TAS</u> (In English)
- Goldade, V. A., Zotov, S. V., Shapovalov, V. M. et al. (2019) Electret effect in polymer nanocomposites (review). *Polymer Materials and Technologies*, 5 (2), 6–18. <u>https://doi.org/10.32864/polymmattech-2019-5-2-6-18</u> (In English)
- Gorokhovatskij, Yu. A. (1991) Termoaktivacionnaya tokovaya spektroskopiya vysokoomnyh poluprovodnikov i dielektrikov [Thermally activated current spectroscopy of high-resistance semiconductors and dielectrics]. M.: Nauka publ., 248 p. (In Russian)
- Gorokhovatskij Yu. A., Demidova N. S., Temnov D. E. (2020) Electric charge relaxation in the polyethylene with mineral inclusions of diatomite. *St. Petersburg Polytechnical State University Journal. Physics and Mathematics*, 13 (2), 9–16. <u>https://doi.org/10.18721/JPM.13201</u> (In English)
- Gorokhovatskij Yu. A., Sotova Yu. I., Temnov D. E. (2022) A study of charge relaxation in corona electrets based on P(VDF-TFE) copolymer. *Physics of Complex Systems*, 3 (3), 104–108. <u>https://doi.org/10.33910/2687-153X-2022-3-3-104-108</u> (In English)
- Guliakova, A., Henderyckx, A., Shishkin, N. et al. (2024) Influence of crystallinity and isotacticity on charge decay of polypropylene homopolymer blends. *IEEE Transactions on Dielectrics and Electrical Insulation*, 31 (5), 2358–2364. <u>https://doi.org/10.1109/TDEI.2024.3417953</u> (In English)
- Kara, Y., Molnár, K. (2021) A review of processing strategies to generate melt-blown nano/microfiber mats for high-efficiency filtration applications. *Journal of Industrial Textiles*, 51, 137–180. <u>https://doi.org/10.1177/ 15280837211019488</u> (In English)
- Kestelman, V. N. (2000) *Electrets in Engineering: Fundamentals and Applications*. New York: Springer Publ., 281 p. <u>https://doi.org/10.1007/978-1-4615-4455-5</u> (In English)
- Kovalenko, M. A., Goldade, V. A. (2021) Electret properties of nanocomposites based on polyethylene and polylactide. In: Proceedings of the 8th International Scientific and Practical Conference "International Forum: Problems and Scientific Solutions". Melbourne: CSIRO Publ., pp. 295–303. (In English)
- Kovalenko, M. A., Goldade, V. A., Zotov, S. V. et al. (2023) Elektretnoe sostoyanie v nanokompozitakh na osnove polilaktida [Electret state in nanocomposites based on polylactide]. *Problemy fiziki, matematiki i tekhniki — Problems of Physics, Mathematics and Technics*, 2 (55), 20–24. (In Russian)
- Li, X., Wang, Y., Xu, M. et al. (2021) Polymer electrets and their applications. *Journal of Applied Polymer Science*, 138 (19), article 50406. <u>https://doi.org/10.1002/app.50406</u> (In English)
- Minzagirova, A. M., Galikhanov, M. F., Khayrullin, R. Z. (2021) Influence of montmorillonite on the change of electret properties of polypropylene. *The VIII International Young Researchers' Conference — Physics, Technology, InnovationS (PTI-2021)*, 2466 (1), article 060023. <u>https://doi.org/10.1063/5.0089012</u> (In English)
- Pinchuk, L. S. (2012) *Melt blowing: Equipment, technology, and polymer fibrous materials*. Berlin: Springer Publ., 224 p. <u>https://doi.org/10.1007/978-3-642-55984-6</u> (In English)
- Xiao, H. (2015) Study on correlation of filtration performance and charge behavior and crystalline structure for melt-blown polypropylene electret fabrics. *Journal of Applied Polymer Science*, 132 (47), article 42807. <u>https:// doi.org/10.1002/app.42807</u> (In English)
- Zhang, J. (2020) Electret characteristics of melt-blown polylactic acid fabrics for air filtration application. *Journal of Applied Polymer Science*, 137 (4), article 48309. <u>https://doi.org/10.1002/app.48309</u> (In English)