Tuning electrical and thermal conductivity of polyurethane-based insulating systems by hallosite nanotube doping

Miloš Kováč[1], *Štefan* Hardoň[1*], *Jozef* Kúdelčík[1], *Marián* Janek[1], and *Vitalii* Bondariev[2]

[1]Department of Physics, Faculty of Electrical Engineering and Information Technology, University of Žilina, Univerzitná 8215/1, 01026 Žilina, Slovakia
[2]Department of Electrical Devices and High Voltage Technology, Lublin University of Technology, 38d Nadbystrzycka St., 20-618 Lublin, Poland

Abstract. The presented work investigates the effect of Halloysite Nanotubes (HNTs) doping on the electrical and thermal transport behavior of polyurethane (PUR) systems designed for advanced electro-insulating applications. Three representative PUR compounds: VUKOL N22, VUKOL N22 Magna Blue, and VUKOL N70 were selected as model matrices due to their established use in encapsulation and potting materials for power electronics. Each system was modified with 2 wt.% and 5 wt.% of HNT nanofillers in order to analyze the extent to which tubular aluminosilicate nanoparticles alter charge conduction and heat dissipation within the polymer bulk. Electrical measurements revealed that the inclusion of HNTs strongly affects the conduction process, primarily through enhanced interfacial polarization, carrier trapping, and modification of percolation pathways between polymer chains. Thermal conductivity analysis showed a moderate but systematic increase, indicating more efficient phonon transport and partial formation of thermally conductive microchannels mediated by well-dispersed nanotubes. The results confirm that controlled HNTs incorporation enables precise tuning of both electrical and thermal properties of PUR systems, offering new perspectives for the design of multifunctional insulation materials with improved dielectric stability and thermal management, particularly suitable for emerging high-voltage, high-temperature, and energy-dense power devices.

1 Introduction

Two-component polyurethane (PUR) resins are widely used as encapsulation and insulating materials in power electronics, high-voltage systems, and aerospace equipment because of their strong dielectric strength, mechanical stability, and resistance to environmental stresses. As operational requirements continue to intensify in the form of higher temperatures, increased electrical loading, and repeated mechanical deformation, conventional PUR formulations are approaching their functional limits. This trend highlights the need for advanced polymer systems whose properties can be deliberately adjusted for multifunctional performance [1 - 4].

A promising strategy for improving the behavior of polymeric insulation involves the incorporation of nanoscale fillers. HNTs, naturally occurring aluminosilicate minerals with a hollow tubular structure, have attracted significant attention due to their low cost, biocompatibility, and favorable surface chemistry. Their outer siloxane and inner aluminol surfaces enable selective interactions, controlled chemical modification, and stable dispersion within polymer matrices. Halloysite may exist in hydrated or dehydrated forms depending on thermal treatment, and this variability influences its interfacial behavior. Although HNTs resemble multi-walled carbon nanotubes in geometric form, they are more environmentally compatible, easier to process, and significantly more cost effective. Their high aspect ratio and characteristic mesoporous architecture support mechanical reinforcement and create tortuous pathways that suppress charge transport while enhancing thermal conduction [5 - 7].

Previous studies have demonstrated that HNTs can improve thermal stability, dielectric robustness, and conductivity behavior in a variety of polymer systems including epoxies, polyethylene, and conducting polymers. These enhancements have been associated with interfacial polarization, modified carrier dynamics, and the formation of filler mediated networks. Recent theoretical and experimental findings emphasize that the interphase surrounding HNTs strongly influences mechanical and electrical behavior, indicating that HNTs act as active structural elements that shape the overall multifunctional response of nanocomposites [5 - 7]. Our earlier investigations involving ZnO, Al_2O_3, SiO_2 and MgO nanoparticle filled polyesterimide and polyurethane systems further confirmed that even low nanofiller loadings can shift dielectric relaxation processes, alter polymer chain mobility, and improve resistive and thermal characteristics [8 - 10].

* Corresponding author: stefan.hardon@uniza.sk

Despite these promising results, the influence of HNTs on commercial two-component polyurethane systems remains insufficiently explored. Most published work concerns thermoplastics or epoxy-based materials, leaving critical questions unanswered regarding the dielectric, thermal, and mechanical behavior of PUR HNT composites processed under industrial curing conditions. Important structure property relationships involving interfacial polarization, filler network formation, and matrix chain dynamics are not yet adequately understood in these widely used commercial PUR systems.

The present study addresses these gaps by evaluating the effect of controlled HNTs loading on the multifunctional performance of commercial polyurethane matrices. Special emphasis is placed on the interplay between nanoscale dispersion quality, interfacial interactions, and their combined influence on electrical conductivity and thermal transport. Since halloysite is naturally abundant and cost effective, its application aligns with both performance driven design and sustainability-oriented objectives. The results presented in this work contribute to the rational development of advanced nanodielectric materials intended for next generation power electronics, energy systems, and mobility technologies.

2 Materials studied

The principal aim of this investigation is to evaluate and compare how the incorporation of HNTs influences the dielectric behavior of three newly developed two-component PUR systems manufactured by VUKI a.s. The commercial formulations examined in this work include VUKOL N22 (Sample A), VUKOL N22u Magna Blue (Sample B), and VUKOL N70/2 (Sample C). These PUR materials are widely applied in the fabrication and protection of electrical components, particularly in processes such as the casting of small and medium power transformers, encapsulation and sealing of capacitors, coils, and other sensitive electronic parts, and the production of prototype components and scale models where rapid demolding is advantageous. They are also employed for potting battery systems, embedding assemblies with dissimilar thermal expansion coefficients, and filling structural cavities in electrical devices where a stress-free insulating compound with high elasticity, robust dielectric properties, and enhanced thermal conductivity is required. Their suitability for electronic encapsulation, cavity filling, and transparent UV-resistant applications further underscores their industrial relevance [11].

HNTs (Sigma-Aldrich, product No. 685445, St. Louis, MO, USA) were introduced into each PUR formulation at loading levels of 2.0 and 5.0 wt%. HNTs are naturally occurring aluminosilicate with the chemical formula $Al_2Si_2O_5(OH)_4 \cdot nH_2O$ and possesses a characteristic multilayer tubular morphology formed through the rolling of kaolinite sheets. The nanotubes typically exhibit inner diameters of approximately 10 to 30 nm, outer diameters in the range of 50 to 70 nm, and lengths extending from several hundred nanometers to multiple micrometers. The presence of hydroxyl groups on both inner and outer surfaces enables diverse physicochemical interactions with polymer chains and allows for targeted functionalization. The high aspect ratio, appreciable specific surface area, and intrinsic thermal stability of HNTs make them effective multifunctional fillers capable of enhancing mechanical integrity, modifying thermal transport, and influencing dielectric response. Their inherent permittivity can also contribute to controlled shifts in the effective dielectric constant of the host matrix.

All nanocomposite samples containing 2.0 and 5.0 wt% HNTs were prepared using a direct dispersion procedure [8 – 10, 12, 13] consistent with methodologies established in our prior work, ensuring uniform filler distribution and reproducible composite structure.

3 Measurement procedures

3.1 Volume conductivity

The determination of volume conductivity (S/m) provides a fundamental indicator of charge transport behavior in polymer nanocomposites and is essential for evaluating their suitability for high-voltage insulation systems. This property quantifies the extent to which the bulk material permits electrical conduction under a sustained direct-current electric field and is highly sensitive to interfacial polarization mechanisms, filler dispersion uniformity, and matrix-nanofiller interactions.

Volume conductivity measurements were performed following the procedures specified in IEC 62631-3-1 and IEC 62631-3-2. A Keithley 6517A electrometer in combination with the Keithley 8009 resistivity fixture (Keithley Instruments, OH, USA) was employed to ensure precise low-current detection and stable electrode contact conditions. Prior to electrical characterization, specimens were short-circuited for 24 hours to minimize transient effects and achieve equilibrium charge distribution. For statistical validation, five separately fabricated samples were evaluated, enabling assessment of measurement repeatability and minimizing variability associated with sample preparation.

For Sample A, the unmodified polyurethane exhibited a volume conductivity of 7.28×10^{-14} S/m, characteristic of insulating-grade PUR systems. Incorporation of 2 wt.% HNTs resulted in a decrease to 8.01×10^{-15} S/m, while the 5 wt.% HNTs formulation further reduced conductivity to 9.26×10^{-15} S/m. These reductions reflect the strong capability of HNTs to impede charge transport through the formation of elongated and highly resistive conduction paths. The decrease in conductivity indicates that interfacial trapping, dipole immobilization, and the presence of deep trap states introduced by the nanotube interfaces significantly suppress long-range carrier mobility.

Table 1. Electrical Volume Conductivity of Polyurethane Samples with and Without HNTs

Material	Conductivity (S.m^{-1})
Sample A	7.28 10^{-14}
Sample A + 2% HNTs	8.01 10^{-15}
Sample A + 5% HNTs	9.26 10^{-15}
Sample B	2.86 10^{-14}
Sample B + 2% HNTs	1.60 10^{-14}
Sample B + 5% HNTs	8.59 10^{-15}
Sample C	8.80 10^{-12}
Sample C + 2% HNTs	2.76 10^{-13}
Sample C + 5% HNTs	1.07 10^{-12}

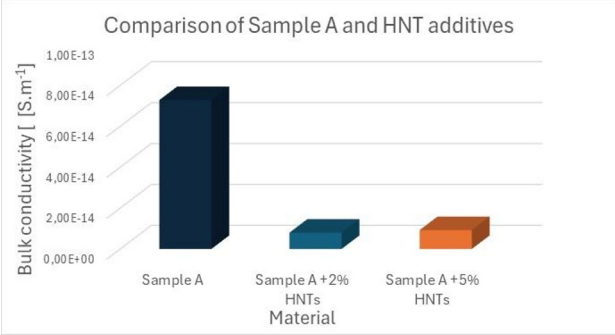

Fig. 1. Volume conductivity of Sample A polyurethane with 0, 2, and 5 wt.% HNT.

Sample B exhibited comparable trends but with even more substantial conductivity suppression. The neat resin showed a conductivity of 2.86 × 10^{-14} S/m. Introducing 2 wt.% HNTs lowered this value to 1.6 0 × 10^{-14} S/m, and the 5 wt.% composite reached 8.59 × 10^{-15} S/m, representing the strongest insulating behavior among the three PUR matrices. The pronounced decrease confirms that the Sample B matrix offers particularly favorable polymer–nanotube interactions, enabling the development of interfacial regions with high polarization potential and deep charge traps. These features significantly extend the time required to reach ohmic conduction, consistent with absorption-controlled transient currents and Maxwell–Wagner–Sillars interfacial processes.

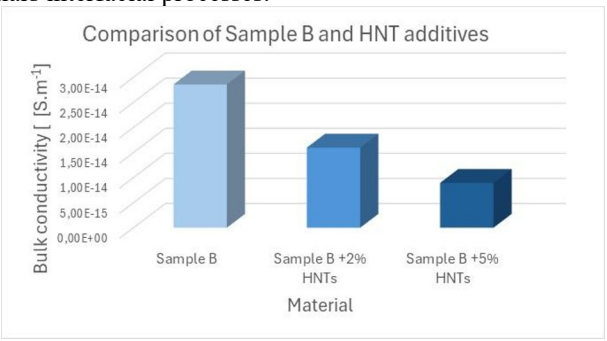

Fig. 2. Volume conductivity of Sample B polyurethane with 0, 2, and 5 wt.% HNT.

In contrast, Sample C demonstrated a distinct response due to its inherently higher baseline conductivity. The unmodified material exhibited 8.80 × 10^{-12} S/m, which is one to two orders of magnitude higher than Samples A and B. Doping with 2 wt.% HNTs substantially reduced conductivity to 2.76 × 10^{-13} S/m, indicating that HNTs incorporation effectively disrupts conductive pathways within this matrix as well. However, at 5 wt.% HNTs, conductivity increased again to 1.07 × 10^{-12} S/m. This reversal suggests the onset of agglomeration phenomena at higher filler loadings, where nanotube clustering locally enhances charge percolation, reduces interfacial areas available for polarization, and compromises the uniformity of the insulating network. Creation of agglomerations also due to the different viscosity value of pure PUR (Sample C).

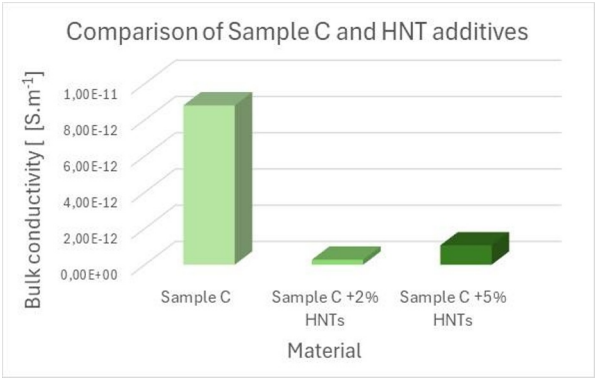

Fig. 3. Volume conductivity of Sample C polyurethane with 0, 2, and 5 wt.% HNT.

Across all three PUR systems, long stabilization times approaching approximately one hour before reaching steady-state current indicate that absorption currents dominate the early phase of the DC measurement. These transient currents are associated with dipolar orientation, charge accumulation at polymer-filler interfaces, and delayed carrier drift within the bulk material. Such behavior is characteristic of highly resistive nanodielectrics that contain extensive interphase regions capable of trapping charge carriers. The composites exhibiting conductivities below 10^{-15} S/m, particularly Sample B with 5 wt.% HNTs and Sample A with 2 respectively 5 wt.% HNTs, can therefore be classified as high-performance insulating materials suitable for demanding applications including high-voltage encapsulation, potting of power electronic modules, and insulation of energy storage components.

3.2 Thermal conductivity

Thermal conductivity is a critical parameter for polymer-based insulating materials used in power electronics, where insufficient heat transport can accelerate thermal aging, induce localized overheating, and compromise dielectric reliability. Even modest improvements in heat dissipation can significantly enhance the operational stability of encapsulated components and extend service lifetime under high thermal and electrical stress.

In this work, thermal conductivity characterization was performed using a custom-built measurement platform specifically developed for polyurethane composite systems [14]. The results were later validated with a TPS 2500 S thermal constants analyzer (Hot Disk AB, Sweden), which provides high-precision evaluation of thermal conductivity, thermal diffusivity, and specific heat capacity in compliance with ISO 22007-2. For each formulation, five consecutive measurements were carried out, and the mean value was reported to ensure statistical robustness and measurement repeatability.

For Sample B (Figure 4, second subplot), the neat PUR exhibits a thermal conductivity of 0.200 $W \cdot m^{-1} \cdot K^{-1}$. Upon incorporation of 2 wt.% HNTs, the conductivity increases to 0.213 $W \cdot m^{-1} \cdot K^{-1}$, and reaches 0.220 $W \cdot m^{-1} \cdot K^{-1}$ at 5 wt.% HNTs. Although the absolute change is relatively small, the monotonic increase is in line with trends commonly reported for solid polymer composites containing thermally conductive fillers. These results indicate that HNTs act as effective modifiers of heat transport in the polyurethane matrix. Similar behavior is observed for samples A and C. In the case of Sample C, the thermal conductivity of the pure sample is much higher (0.51 $W \cdot m^{-1} \cdot K^{-1}$) than that of Samples A and B, but the trend remains similar.

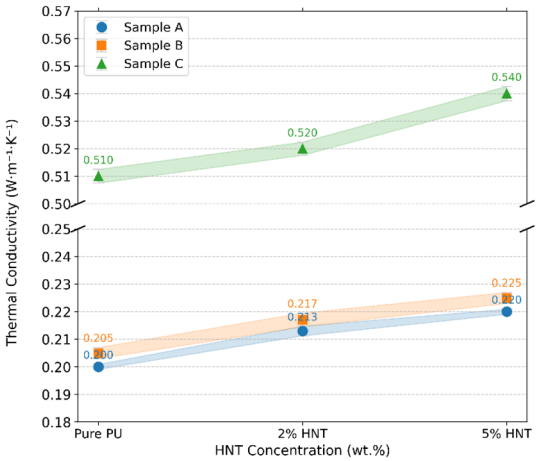

Fig. 4. Thermal conductivity of PUR/HNT composites. The data points represent the mean of 10 measurements, and the shaded area indicates the confidence band corresponding to the standard error of the mean.

The enhancement in thermal conductivity is primarily associated with the intrinsic thermal properties of the HNTs and their ability to establish preferential pathways for phonon transport within the composite. Owing to their higher thermal conductivity compared to the host polymer and their tubular morphology, HNTs can participate in the formation of partial heat conduction networks that facilitate energy transfer across the material volume. Literature reports support the formation of such filler-mediated conduction paths in halloysite-based composites, where nanotubes promote more continuous routes for phonons, which are the dominant heat carriers in these systems.

From a statistical viewpoint, the increase in thermal conductivity with rising HNTs content is small but measurable. Analysis of repeated measurements shows that the mean values for 0, 2, and 5 wt.% HNTs exhibit limited overlap of their confidence intervals, indicating that the observed evolution is not solely attributable to measurement scatter. This behavior supports the interpretation that HNTs contribute to a progressively more interconnected thermal transport network in Sample B, even at relatively low filler concentrations.

4 Conclusion

The incorporation of HNTs significantly influenced the multifunctional performance of the investigated PUR systems. For electrical conductivity, all three PUR matrices exhibited a marked decrease when modified with 2 wt.% and 5 wt.% HNT, confirming that the nanotubes effectively suppress charge transport through enhanced interfacial trapping and the formation of conduction pathways. The lowest conductivities were achieved in Sample B and Sample A, both at 5 wt.% HNT, positioning these formulations as high-grade insulating materials.

For thermal transport, Sample B showed a modest but consistent increase in thermal conductivity from 0.200 $W \cdot m^{-1} \cdot K^{-1}$ for the neat resin to 0.213 $W \cdot m^{-1} \cdot K^{-1}$ and 0.220 $W \cdot m^{-1} \cdot K^{-1}$ at 2 wt.% and 5 wt.% HNTs, respectively. This trend indicates the formation of partial phonon-conducting pathways introduced by the nanotubes. Despite the significantly higher thermal conductivity of the pure Sample C (0.51 $W \cdot m^{-1} \cdot K^{-1}$) compared to Samples A and B, a similar overall behavior is observed for all samples.

Overall, the results demonstrate that controlled HNTs loading can simultaneously reduce electrical conductivity and enhance thermal conductivity, which is a desirable combination for advanced encapsulation and high-voltage insulation applications. [12, 13].

Acknowledgements: This work was supported by Slovak Research and Development Agency under the contract No. APVV-21-0078 and Visegrad Fund through the Visegrad Scholarship program under ID: 52510078.

References

1. V. Mentlík, O. Michal, Influence of SiO2 nanoparticles and nanofibrous filler on the dielectric properties of epoxy-based composites, Mater. Lett. **223**, 41–44 (2018). https://doi.org/10.1016/j.matlet.2018.04.021.
2. P. Havran, R. Cimbala, B. Dolník, M. Rajňák, R. Štefko, J. Király et al., Dielectric relaxation spectroscopy of hybrid insulating nanofluids in time, distribution, and frequency domain, J. Mol. Liq. **409**, 125409 (2024). https://doi.org/10.1016/j.molliq.2024.125409.
3. S.B. Khan, S. Chen, X. Sun, Advancements in polymer nanocomposite manufacturing: revolutionizing medical breakthroughs via additive manufacturing, Polym. Bull. **81**, 9465–9517

(2024). https://doi.org/10.1007/s00289-024-05154-8.

4. S. Bucko, J. Király, R. Cimbala, Dielectric response at different nanoparticle concentrations for GTL oil-based magnetic nanofluids, Acta Polytech. Hung. **22**, 63–80 (2025).
5. J. Hornak, P. Kadlec, R. Polanský, Halloysite nanotubes as an additive to ensure enhanced characteristics of cold-curing epoxy resins under fire conditions, Polymers **12**, 1881 (2020). https://doi.org/10.3390/polym12091881.
6. C. Cheng, W. Song, Q. Zhao, H. Zhang, Halloysite nanotubes in polymer science: purification, characterization, modification and applications, Nanotechnol. Rev. **9**, 323–344 (2020). https://doi.org/10.1515/ntrev-2020-0024.
7. M. Fahimizadeh et al., Halloysite clay nanotubes: Innovative applications by smart systems, Appl. Clay Sci. **251**, 107319 (2024). https://doi.org/10.1016/j.clay.2024.107319.
8. J. Kúdelčík, Š. Hardoň, P. Trnka, O. Michal, J. Hornak, Dielectric responses of polyurethane/zinc oxide blends for dry-type cast cold-curing resin transformers, Polymers **13**, 375 (2021). https://doi.org/10.3390/polym13030375.
9. Š. Hardoň et al., Fabrication and broadband dielectric study of properties of nanocomposites materials based on polyurethane, IEEE Access **12**, 114227–114241 (2024). https://doi.org/10.1109/ACCESS.2024.3443462.
10. Š. Hardoň et al., Influence of nanoparticles on the dielectric response of a single component resin based on polyesterimide, Polymers **14**, 2202 (2022). https://doi.org/10.3390/polym14112202.
11. VUKI a.s., Products, https://www.vuki.sk/produkty (accessed 21 November 2025).
12. O. Michal, V. Mentlík, J. Hornak, Impact of ultrasonic mixing on the electrical properties of PEI/SiO_2 nanocomposites, AIP Conf. Proc. **2411**, 050010 (2021). https://doi.org/10.1063/5.0066867.
13. J.V. Džunuzović et al., Fabrication of polycaprolactone-based polyurethanes with enhanced thermal stability, Polymers **16** (2024). https://doi.org/10.3390/polym16131812.
14. M. Janek, J. Kúdelčík, S. Hardoň, M. Gutten, Novel, cost effective, and reliable method for thermal conductivity measurement, Sensors **24**, 7269 (2024). https://doi.org/10.3390/s24227269 .