Thermomechanically modified ground tire rubber/zinc borate compositions as fillers for flexible polyurethane foams

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AIM OF THE PROJECT

- Development of method for material recycling of ground tire rubber (GTR),
- Development of the continuous method for GTR modification enabling its efficient utilization in polymer composites,
- Manufacturing of foamed polyurethane(PU)/GTR composites with potential use of insulation or damping materials,
- Enhancement of thermal stability and reduction of flammability of foamed PU/GTR composites,

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BACKGROUND

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POLYURETHANE FOAMS

- Global demand for polyurethanes ~20.4 milion tons, ~59% accounts for foams, ~31% for flexible foams,
- Applied in the furniture, automotive, construction, packaging industries, as well as damping and soundproofing materials,
- Crucial direction of development pronounced by producers - increasing the functionality, reducing waste generation, or reducing materials' costs,
- It is essential to provide beneficial cellular structure, which determines the mechanical, thermomechanical and insulation performance,

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BACKGROUND

GROUND TIRE RUBBER

- In Europe, almost 3.3 million tons of car tires are being withdrawn from use annually,
- The European Union's primary method is material recycling (accounting for ~40% of car tire recycling),
- The most popular is the shredding of tires, resulting in ground tire rubber (GTR),
- Application of GTR enables lowering of materials' costs,
- Also, it may enhance various materials' parameters, e.g., tensile strength, toughness, or sound absorption properties,
- Interesting candidate for PU foamed materials - lower thermal conductivity coefficient of GTR compared to solid PU (~160 and ~220 mW/(m·K),
- Although, it may require modifications to increase surface roughness and improve interfacial adhesion,

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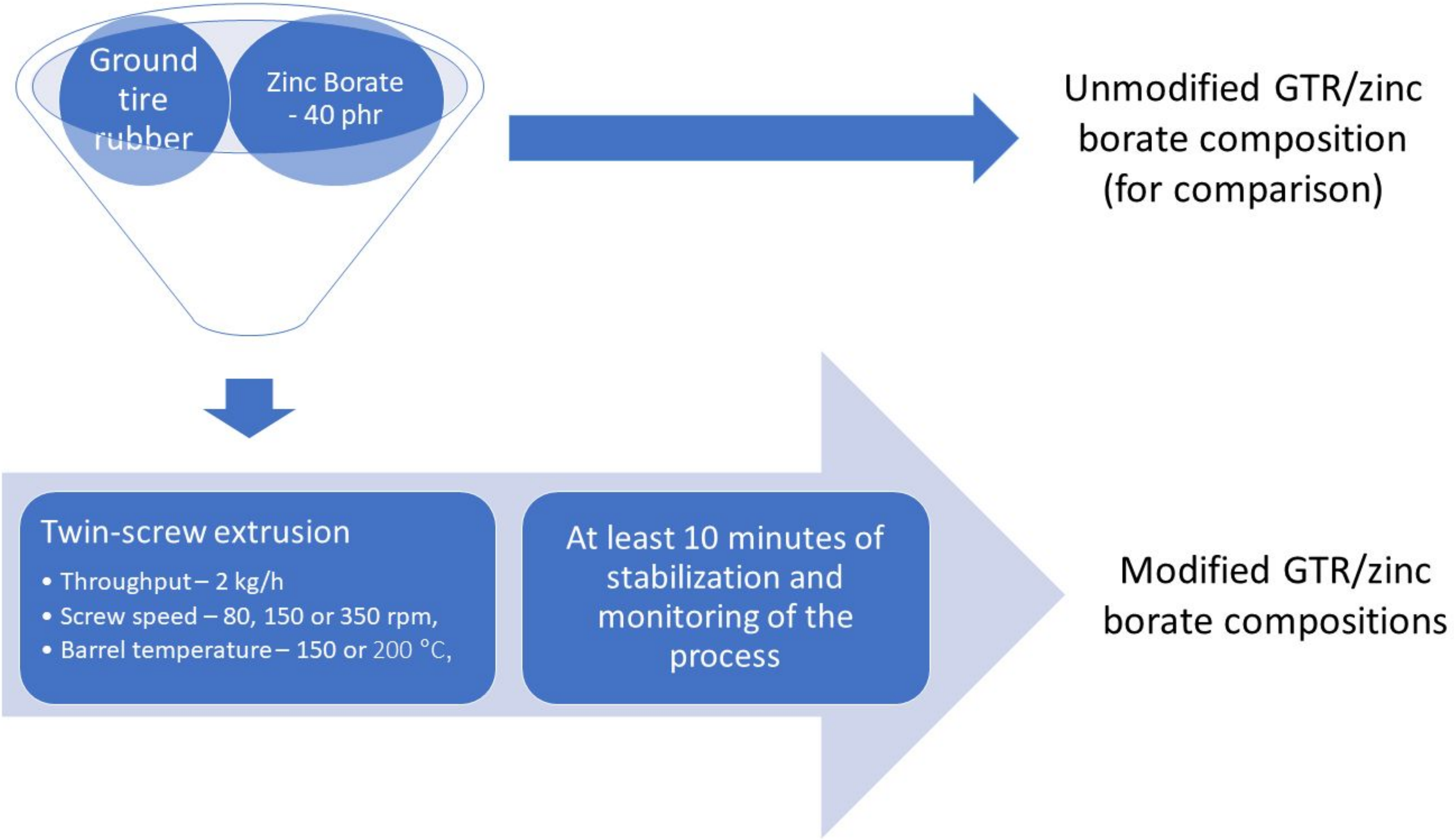
GTR Modification Procedure



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Modified GTR Particle Size

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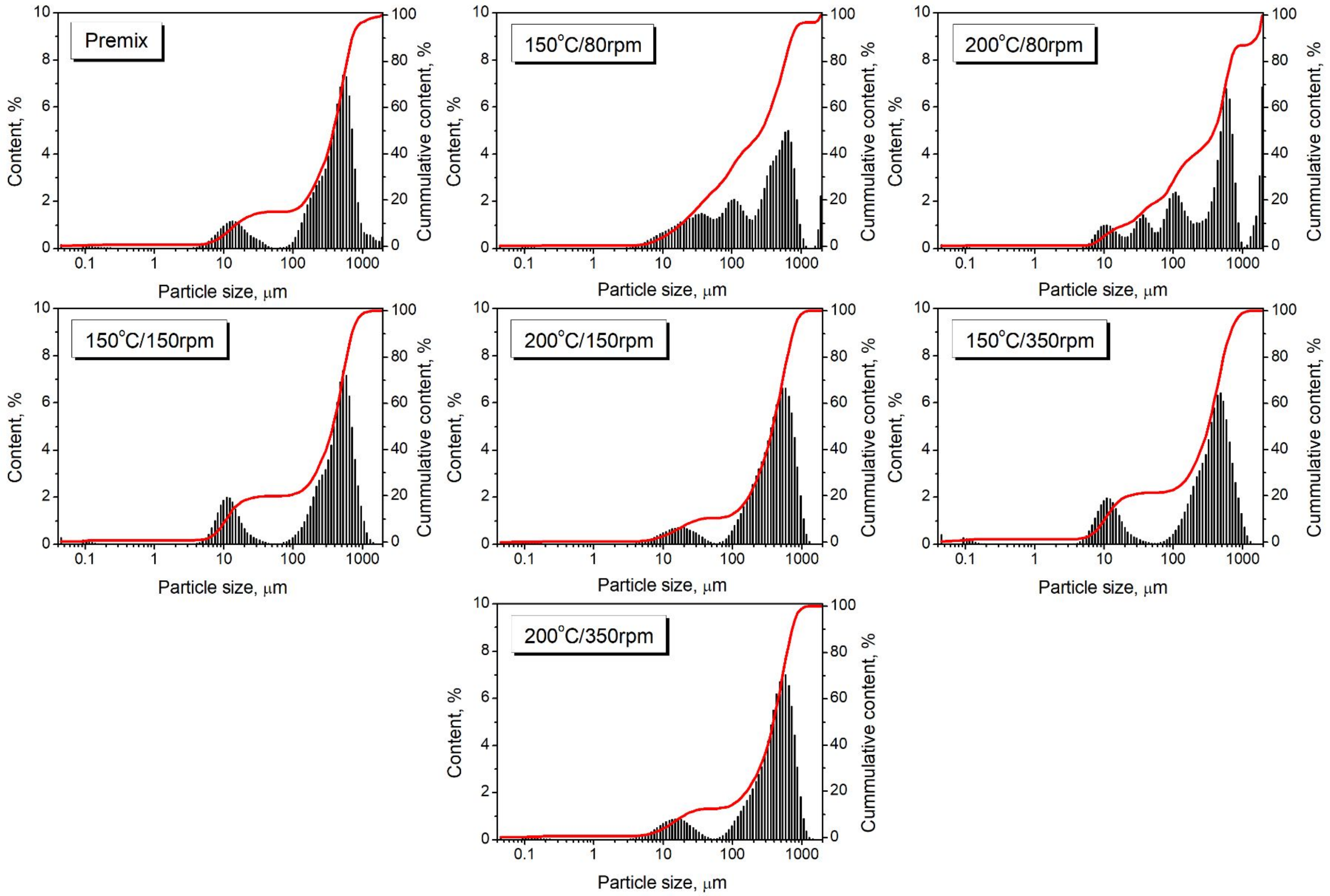

Preparation of PU Composite Foams

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Preparation of prepolymer

- PTMG polyol,
- TDI isocyanate,
- 60 °C, 120 min,
- NCO content – 18.2%,

Preparation of polyol blend

- Mixing of polyols, catalysts, foam stabilizer, blowing agent and GTR,
- Homogenization of GTR with polyol to improve dispersion,

Mixing and polymerization

- Mixing of prepolymer with polyol blend,
- Pouring into heated mold,
- Demolding and conditioning,

Foams' Cellular Structure

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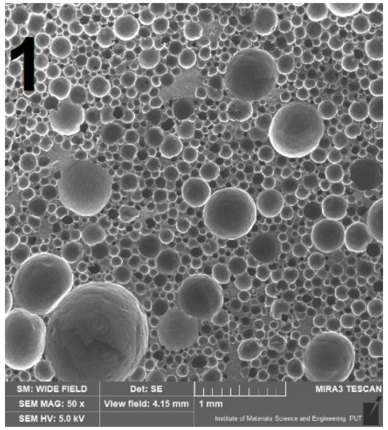
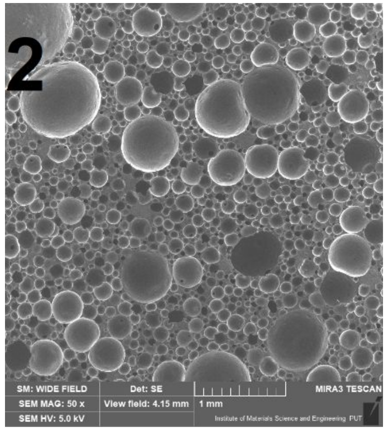
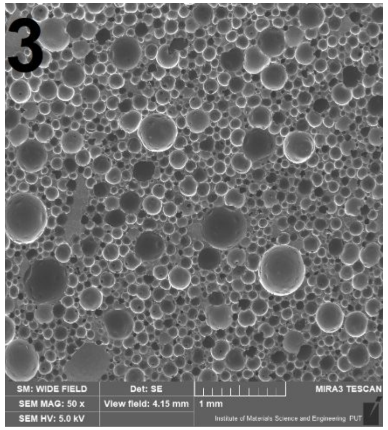


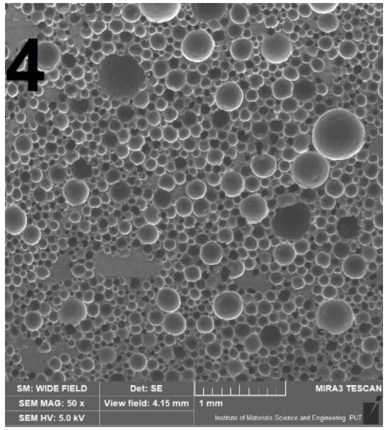
192 μm
Premix



186 μm
150 °C/80 rpm



172 μm
200 °C/80 rpm



166 μm
150 °C/150 rpm

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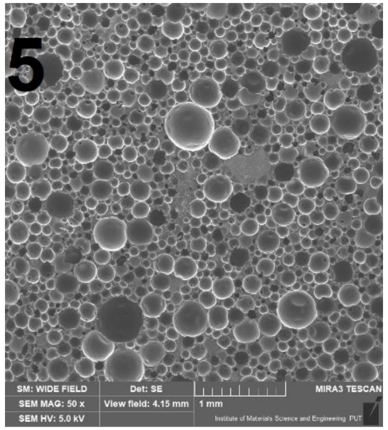
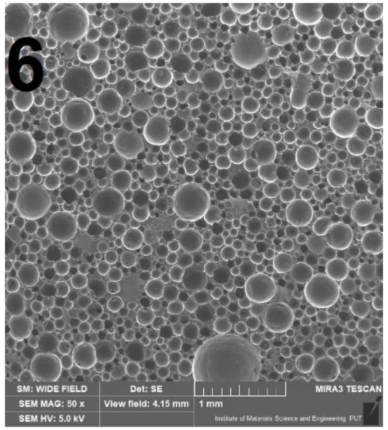
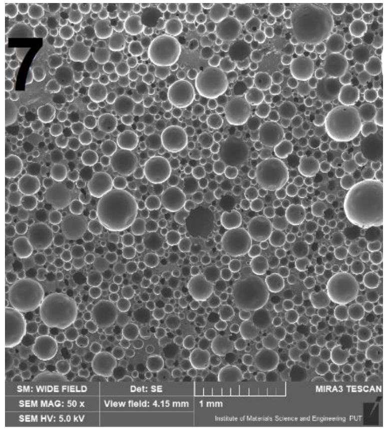


163 μm
200 °C/150 rpm



160 μm
150 °C/350 rpm



163 μm
200 °C/350 rpm

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Foams' Cellular Structure

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Parameter	Premix	150 °C/80 rpm	200 °C/80 rpm	150 °C/150 rpm	200 °C/150 rpm	150 °C/350 rpm	200 °C/350 rpm
Average cell size, µm	192 ± 116	186 ± 106	172 ± 98	166 ± 91	163 ± 86	160 ± 83	163 ± 90
Circularity	0.35 ± 0.21	0.36 ± 0.23	0.50 ± 0.27	0.51 ± 0.27	0.54 ± 0.27	0.54 ± 0.24	0.59 ± 0.27
Aspect ratio	1.34 ± 0.31	1.32 ± 0.24	1.32 ± 0.27	1.31 ± 0.22	1.29 ± 0.22	1.29 ± 0.19	1.29 ± 0.23
Roundness	0.78 ± 0.15	0.78 ± 0.12	0.78 ± 0.12	0.78 ± 0.12	0.80 ± 0.12	0.79 ± 0.11	0.79 ± 0.12
Open cell content, %	57.66	57.07	54.54	54.31	53.15	56.13	59.29
λ coefficient, mW/(m·K)	69.15	66.65	65.56	68.21	64.97	68.63	69.16

Foams' Mechanical Performance

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Parameter	Premix	150 °C/80 rpm	200 °C/80 rpm	150 °C/150 rpm	200 °C/150 rpm	150 °C/350 rpm	200 °C/350 rpm
Tensile strength, kPa	701 ± 112	993 ± 104	1009 ± 93	974 ± 10	802 ± 19	1019 ± 81	915 ± 43
Elongation at break, %	152 ± 42	156 ± 14	152 ± 10	163 ± 12	175 ± 6	160 ± 10	150 ± 3
Toughness, J/cm^3	71.8 ± 24.4	91.4 ± 18.4	92.1 ± 16.3	92.4 ± 2.3	76.6 ± 1.5	99.2 ± 21.5	79.6 ± 5.7
E' at 25 °C, MPa	1.94	5.34	5.40	3.96	4.45	5.23	5.24
T_g of GTR, °C	-49.2	-49.8	-48.3	-50.0	-49.3	-48.5	-48.6
T_g of PU foam, °C	19.7	33.9	32.3	26.3	21.4	24.9	25.3

Foams' Thermal Stability

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Sample	$T_{-2\%}$, ˚C	$T_{-5\%}$, ˚C	$T_{-10\%}$, ˚C	$T_{-50\%}$, ˚C	T_{max1}, ˚C	T_{max2}, ˚C	Residue, wt%
Premix	242.2	261.1	281.5	418.3	286.3	424.3	10.85
150 °C/80 rpm	246.5	261.8	280.1	416.5	268.6	423.3	11.61
200 °C/80 rpm	246.2	263.8	282.5	419.2	267.4	424.0	10.85
150 °C/150 rpm	247.6	263.1	282.3	419.2	264.2	423.0	11.85
200 °C/150 rpm	249.1	263.8	284.4	420.2	268.4	424.3	11.97
150 °C/350 rpm	248.1	264.7	285.2	420.8	269.1	424.3	11.64
200 °C/350 rpm	248.8	266.1	286.4	421.3	271.2	424.9	12.20

Foams' Sound Absorption Performance

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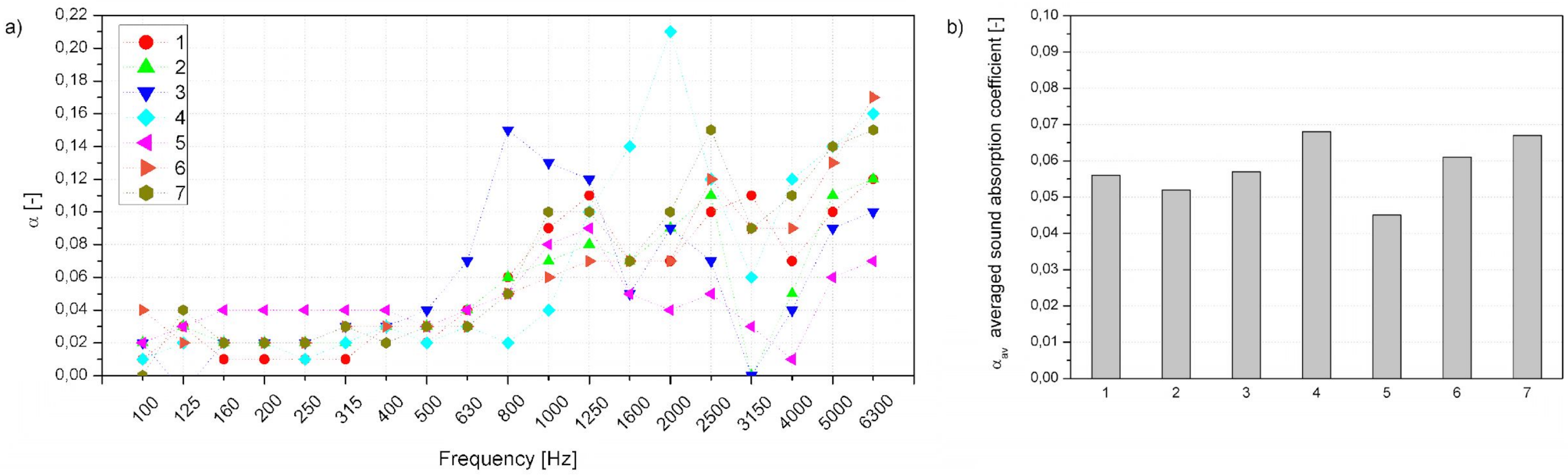

Conclusions

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- Modification of GTR with zinc borate enable reduction of particle size and increase of roughness of GTR particles surface,
- It yielded higher homogeneity of foams' cellular structure and enhanced composites' performance,
- Enhancement of insulation performance was noted,
- Higher GTR roughness improved interfacial adhesion and increased composites' strength,
- Thermal decomposition onset was shifted towards higher temperatures,
- Sound absorptio coefficient was hardly affected, pointing to the need for more substantial modifications of cellular structure.

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