RESEARCH ARTICLE

Polystyrene nanofibers for nonwoven porous building insulation materials

Vitaliy Datsyuk, Svitlana Trotsenko, Katharina Peikert, Katja Höflich, Nelli Wedel, Christian Allar, Torben Sick, Victor Deinhart, Stephanie Reich, Wolfgang Krcmar

1Fachbereich Physik, Institut für Experimental Physik, Freie Universität Berlin, Berlin, Germany
2Micromeritics GmbH, Unterschleißheim, Germany
3Nanoscale Structures and Microscopic Analysis Lab, Helmholtz-Zentrum Berlin für Materialien und Energie, Berlin, Germany
4Faculty Materials Engineering, Technische Hochschule Nürnberg - Georg Simon Ohm, Nuremberg, Germany
5Schock GmbH, Regen, Germany

Correspondence
Vitaliy Datsyuk, Fachbereich Physik, Institut für Experimental Physik, Freie Universität Berlin, 14195 Berlin, Germany.
Email: datsyuk@zedat.fu-berlin.de

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The building industry makes a great effort to reduce energy consumption. The use of nanotechnology is one of the approaches to surpassing the properties of conventional insulation materials. In this work, an industrial cost-effective method to manufacture highly porous materials with excellent thermal insulation properties is described. The materials are prepared from polystyrene recovered from the building sector and electrospun as nanofiber-based sheets. Varying electrospinning parameters allow controlling the morphology of the produced materials. The materials are obtained with differences in interfiber and inner-fiber porosity and morphology. The thermal conductivity of the freestanding and compressed materials is evaluated. Those differences affect the insulation performance: the materials with higher interfiber porosity show better thermal insulation in the freestanding state. An increase of the inner-fiber porosity leads to better insulation in the compressed samples. Insertion of carbon nanomaterials reduces the effects of the infrared Radiation. Nanofiber-based insulation materials from the recycled expanded polystyrene (EPS) show thermal conductivity values of 20 to 25 mW/mK (ie, 20% to 30% below the thermal conductivity of the commercial EPS). The effect of integrating polystyrene nanofiber sheets into conventional wall-building materials is also investigated in terms of thermal insulation. The nanofiber insulation sheets are sandwiched between two pieces of the building materials resulting in a drastic increase of the insulation effect. The materials have a great potential in using, for example, as thermal insulation for the restoration of historic buildings in the narrow central parts of the old towns.

KEYWORDS
building insulation, nanofibers, recycling materials, thermal conductivity

1 INTRODUCTION

Due to the strict sustainability standards, the building industry has worked on new concepts for reducing the consumption of petrochemicals and carbon emission over the last decades.1-4 In addition to the application of wood, palm, wool, and...
cellulose fibers as a natural source in the building insulation, new systems with optimized energy consumption have been developed.\textsuperscript{5-8} Vacuum insulation panels (VIPS) and aerogels have been proven to be among the best thermal insulation solutions due to their extremely low thermal conductivity.\textsuperscript{9,10} However, both materials are very costly and have some restrictions in building insulation applications. VIPs have difficulties in the perforation of the material to the building site. Cutting VIP is difficult technically.\textsuperscript{11} Additionally, the vacuum efficiency fades over time due to the air and moisture penetration through the VIP envelope. The synthesis of aerogels is a complex multistage process, which requires stages of sol formation, gelation, surface hydrophobization, due to their extreme hydrophilicity, and drying.\textsuperscript{12,13} Pure aerogels have weak mechanical stability and must be enforced with organic or inorganic binder or envelope, which reduces their insulation performance.\textsuperscript{14} There is, hence, a demand for the development of alternative robust and low-cost materials capable of satisfying the building insulation requirement by significantly reducing the heat flow through the walls.

The waste panels produced by the building industry represent one of the main challenges of the sustainability of building insulation. The yearly consumption of the expanded (EPS) and extruded (XPS) polystyrene (PS) is on the range of 300 to 340 kt.\textsuperscript{15} Only around 10\% of this material is nowadays made from recycled materials.\textsuperscript{16} Large amounts of recyclable PS are produced during the refurbishment of old buildings. About 8 million tons of plastic are released into the ocean yearly\textsuperscript{17} and PS is one of the most prevalent polymers, which is found in the marine surface water.\textsuperscript{18} Increasing the applications of the recycled waste EPS via nanofiber electrospinning is a great approach for its sustainable use in building insulation, in contrast to the difficulties of reusing it in polymer foam production.

Highly porous materials are currently of great interest in thermal insulation applications.\textsuperscript{19-22} According to the study of Spagnol et al,\textsuperscript{23} the main contribution to the thermal insulation efficiency of nanomaterials is gas conduction (62\%), contrary to solid conduction (24\%), and radiation (14\%). For heat insulation in air, pores of diameters smaller than the mean free path of the gas molecules lead to the Knudsen effect,\textsuperscript{24} which further reduces the thermal conductivity due to pores of very small size. Thus, nanotechnology is widely used for the development of new thermal insulation materials.\textsuperscript{25} Moreover, Russel reported\textsuperscript{26} that thermal conductivity is greater for material where solids build continuous phase and have spherical pores than for material where solids have fibrous structure and air as the continuous phase. This is confirmed by the wide-spread use of fibrous insulation materials (mineral wool, glass wool, and natural fibers).\textsuperscript{6,27} For a better performance of the fibrous structures with open pores, electrospinning may be one of the cost-effective methods for drawing nanofibers in industrial-scale volumes.\textsuperscript{28} Electrospinning employs an electric field to charge the free surface of a polymer solution to a relatively high voltage. It results in a stretched jet, which starts spinning, thinning, and, finally, forming polymer fibers on the collector with diameters on the order of tens of nanometers up to submicron size.\textsuperscript{29} Materials produced by electrospinning exhibit a specific surface area from 13 to 98 m\textsuperscript{2}/g.\textsuperscript{30} Polymer nanofibers are used in many applications\textsuperscript{31}: in filtration,\textsuperscript{32} drug delivery,\textsuperscript{33} tissue engineering,\textsuperscript{5} solar cells,\textsuperscript{34} lithium ion batteries,\textsuperscript{35} and as reinforcing\textsuperscript{36} and toughening\textsuperscript{37} additives in composites. It is easy to produce nanofibers filled with particles, such as carbon nanotubes\textsuperscript{38} and carbon black (CB), ceramics, pigments, and other nanofillers.\textsuperscript{39,40} Gibson et al\textsuperscript{41} compared the thermal insulation of the electrospun polycrylonitril (PAN) nanofibers with textile materials. In case of PAN nanofibers, thermal insulation was greatly increased with the simultaneous decrease of the weight and size of protective clothing. Researchers have reported differences in the properties of the electrospun polymer nanofibers depending on their morphology.\textsuperscript{42} For example, it has been reported that nanofibers have higher shear moduli compared to the shear moduli of the corresponding bulk polymers.\textsuperscript{43} This is explained by the low fiber diameters, where polymer chains have stretched macromolecular conformation and modified surface morphology. Different morphologies of nanofibers may be achieved by changing the electrospinning parameters.\textsuperscript{44,45} Variation of the applied electric field, flow rate, or distance from the injector to the collector leads to the changes in the diameter of nanofibers or generating beads in the nanofiber structures.\textsuperscript{46} Difference in the diameter influences nanofiber packaging in material. Nanofibers with higher diameter generate pores with larger diameter of the interfiber galleries.\textsuperscript{47} It is also known that, during the electrospinning solution interaction, the polymer-solvent system can vary dramatically, changing the morphology of nanofibers. Solvents with a high and low boiling point or solvents with different solubility parameters may help to generate materials with significant differences in the surface morphology and porosity.\textsuperscript{48-51} It is also reported that surface porosity can be varied by the relative humidity of the environment or by use of polymers with different molecular weight.\textsuperscript{52} Dayal et al\textsuperscript{53,54} theoretically studied the dependency of fiber morphology on the solvent evaporation in the polymer-solvent system, on the phase separation and on the solvent evaporation in the mixture. They simulated different morphologies from smooth hollow fibers to the porous surfaces on both sides: the surface and in the core. Changes in the fiber surface morphology can be generated by variation of the polymer concentration, the temperature, and the ratio of the solvent evaporation to the phase separation. If the polymer-solvent system forms an unstable two-phase area and the evaporation of the solvent is slower relative to phase separation, the nanofiber surface becomes porous. Pai et al\textsuperscript{55} have experimentally confirmed the ability
to systematically produce nanofibers with intended surface porosity by using dimethyl formamide (DMF) – PS systems. The authors explained such phenomena by the effect of the humidity of the environment, which acts as nonsolvent. The solidification process occurs faster than phase-separation, leading to the formation of highly porous systems. Thus, PS nanofiber sheets can be an alternative to EPS.

In this work, the assessment of three waste PS nanofiber materials is presented: single (DMF); mixed (DMF: dichloromethane (DCM)); and PS nanofibers filled with CB and multiwalled carbon nanotubes (MWNTs). The first two materials were prepared under variable electrospinning conditions to demonstrate the effect of the nanofiber morphology on their insulation properties. Nanofiber morphology and porosity were deeply evaluated based on the materials' efficiency when used as an innovative free-standing material, as well as in combination with conventional building materials.

This paper is organized as follows. Section 2 gives an overview of the materials and methods, which were applied during production and testing waste PS nanofiber sheets. The morphology of our materials is evaluated in Section 3 with a focus on the morphological differences with varying fabrication parameters. The remainder of Section 3 describes the insulation behavior under ambient conditions and applied pressure, followed by a discussion on the use of waste PS nanofiber sheets in combination with conventional building materials. Section 4 summarizes the paper and presents our conclusions.

2 | EXPERIMENTAL SECTION

2.1 | Materials

Waste PS (PS-600) was supplied by Jackson GmbH. DCM, N,N-DMF (Carl Roth GmbH) were used as received without further purification. CB F-101 was kindly supplied by Orion Engineered Carbon S.A. Multiwalled carbon nanotubes (MWCNTs) Baytubes® C 150 P were purchased from Bayer Materials Science AG. Acronal S720 was kindly supplied by BASF SE. A defined fly ash mixture (Microsit®), containing fly ash fraction with a maximum grain diameter of 10 μm, was purchased from BauMineral GmbH. Quartz sand with a grain size distribution of between 0.1 to 0.6 mm and Kaolin (KBE-1) were purchased from Amberger Kaolinwerke Eduard Kick GmbH. Waterglass Betol 39-T (Woellner GmbH) and sodium hydroxide pellets (AppliChem GmbH) were used as received without further purification. Zinc powder (STANDART® Zinc Flake AT) was kindly supplied by Eckart GmbH.

The clay to produce brick samples was kindly supplied from Ceramix AG. Lime-Sandstone samples, thermal insulation plaster, and thin bed mortar were purchased from Baustoff-Union GmbH. The porous concrete samples were obtained from Xella Deutschland GmbH.

2.2 | Electrospinning waste PS

PS solutions with the same concentration of 15 wt percentage were prepared by dissolving of PS into DMF, and DMF/DCM (w:w 1:3), respectively. The solutions were vigorously stirred for 24 h before further use. The 5% CB (w/w) was dispersed in the DMF by a tip-ultrasonicator SONOPULS HD3200 (Bandelin GmbH) and mixed with the polymer solution. MWCNT were dispersed in DMF by use of Acronal S720 (1% wt) in water, dried, and redispersed in DMF. Fabrication of the PS and PS-CB fibers was performed on the commercially available YFlow Industrial Electrospinning Device equipped with four injection heads. In a typical experiment, the PS solution was loaded into a four 20 ml syringes connected by cables to the four injectors with 20 steel needles. Each solution was electrospun with a constant flow rate 4 ml/h and at voltage 40 kV in the X-Y motion mode resulting in nanofiber sheets of 1600 per 2000 mm and thickness of 1 mm, which were collected on a stainless-steel plate. All experiments were carried out at 22°C, relative humidity 45%. The distance between the collectors and injectors was adjusted and fixed as 30 cm. Express tests on the fiber formation were made using optical microscopy (Nikon Eclipse LV 100). The nanofiber sheets of the electrospun materials were then dried at 70°C in the oven.

2.3 | Morphological study

Gas displacement pycnometry (GDP) measurements to investigate the density of the electrospun samples were carried out using a Micromeritics AccuPyc 1340. Analysis temperature was 267 K, and helium was used as displacement medium. Nitrogen sorption experiments were conducted using a Micromeritics 3Flex Surface Analyzer after degassing the samples for 12 h at 303 K under a turbomolecular pump vacuum. The measurement temperature was 77 K. Specific surface areas were calculated using the BET model, applied in the relative pressure range from 0.07 to 0.3. The pore size distribution
was calculated using the BJH model, applied at the desorption branches using Halsey thickness curves as reference and Faas correction. Mercury intrusion porosimetry (MIP) was undertaken with a Micromeritics AutoPore V 9620 at 293 K operated from vacuum to 418 MPa. Samples were degassed in situ prior to measurement. A contact angle of 140° and surface tension of 485 dynes/cm for mercury and a scan rate of $2.5 \times 10^{-3}$ s·ml/g were applied.

Transmission electron microscopy (TEM) was performed on the FEI Tecnai G220 S-Twin machine operating at accelerating voltage 160 kV. The samples of fibers were deposited directly onto copper grids during the process of electrospinning.

Scanning electron microscope (SEM) was carried out using a Zeiss Merlin KMAT instrument at very low acceleration voltages and currents. Thereby, the typical metallic coating of the nonconductive surface could be avoided and, hence, the pristine surface structure was accessible. Still, minor charging artifacts occurred; however, these were avoided by using helium ion beam microscopy (HIM) in a Zeiss Orion Nanofab instrument. Helium gas atoms are ionized of gas atoms at a sharp tip consisting of three only (trimer). Only of the atoms is used for imaging, realizing spot sizes below 1 nm. The secondary electrons escaping from the sample surface are detected and form the image, whereas the introduced positive charge can be compensated by an electron flood gun. This allows for high-resolution imaging of nonconductive samples.

### 2.4 Thermal transport in freestanding nanofiber sheets

Thermal transport properties of the free-standing nanofiber sheets were analyzed with a Hot Disk Transient Plane Source TPS 2500S thermal conductivity analyzer (5501 sensor with $R = 6.4$ mm). For each sample, at least 20 evaluations were performed with the average measurement error 2%. For all analysis, temperature was kept $23^\circ$C and humidity was in range 42 to 45%. Pressure-dependent studies were performed by applying a defined pressure on the top of the analyzing surface (60 per 100 mm) during the thermal conductivity measurements. The pressure was fixed 10 min prior to the measurement in order to stabilize the compressing effects on the interfiber porosity.

### 2.5 Preparation of building material samples

The efficiency of the nanofiber insulation materials (NIMs), in combination with conventional building materials, was evaluated by sandwiching NIM between two slabs of the building materials: lime sandstone, geopolymer, thin-bed mortar, brick, thermal insulation plaster, aerated concrete, and foamed geopolymers. Samples were produced according to the following procedures.

#### 2.5.1 Lime sandstone

Slabs of commercially available lime sandstone were cut out and their surfaces subsequently ground in parallel.

#### 2.5.2 Geopolymer

The activator solution, a mixture of water glass with a solid content of 36 wt-% and sodium hydroxide, was prepared by the following procedure. NaOH pellets were added to the water glass (pH = 11.3) in the ratio 0.233. The mixture was thoroughly mixed for 24 h to completely dissolve the NaOH. Then, the activator solution was mixed with fly ash in a mass ratio of 1:2. Quartz sand was added to the mixture, which was further mixed to achieve a uniform distribution of the sand. After mixing, the mass was poured into corresponding molds at 85°C for 48 hours, whereas the aluminosilicate network formed. After removal from the molds, the samples were wet ground and then redried.

#### 2.5.3 Thin-bed mortar and thermal insulation plaster

Thin-bed mortar and thermal insulation plaster were mixed according to the user manual and poured into silicone molds to form slabs. After demolding and a curing time of 14 days, the specimens were cut to size, ground plane-parallel, and re-dried.

#### 2.5.4 Bricks

A conventional brick clay without further additives was used to produce the brick slabs. The clay was adjusted to a water content of 21 wt-% and aged over a period of one week. The clay was then extruded into slabs (Figure 1A), which were then dried and fired at a maximum firing temperature of 950°C. The brick slabs were then cut and parallel grinded to the exact dimensions $L \times W = 10.0$ cm x 10.0 cm with variable sample thickness (Figure 1B).
2.5.5  |  Aerated concrete

Aerated concrete samples were produced. Corresponding test specimens were cut to size and ground plane-parallel.

2.5.6  |  Foamed geopolymers

91.0 g of waterglass, 12.4 g NaOH were placed into 20.8 g of water to generate an activator solution. The production process is the same as described in paragraph 2.4.2. A dry metakaolin-zinc powder mixture (100 g metakaolin and 1.3 g zinc powder) was then added to the activator solution and mixed with a stirrer for four minutes. The resulting mixture was poured into molds, which were shaken for five minutes to remove incorporated air bubbles. The molds were then stored at room temperature for 2 hours to start foaming via hydrogen release. After the foaming process, samples were self-solidified and geo-polymerized for five days.

2.6  |  Thermal conductivity of building materials

Steady-state thermal conductivity was measured according to DIN EN 1946–2 and ISO 8302:1991 using the guarded hot plate apparatus. The samples (100 per 100 mm) were fixed between two plates with a fixed temperature gradient $\Delta T = 10^\circ C$. The thermal conductivity was calculated from the temperature rise of the cold plate. The measurement error was 2%. For each series, the number of measured samples was limited to two, as the extensive time required per measurement was very high.

2.7  |  Preparation of sandwich samples

After determining the thermal conductivities $\lambda_{10\text{dry}}$, the building material slabs were sawn through perpendicularly to the heat flow direction. By inserting 1, 2, or 3 layers of a PS nanofiber mat, a “sandwich-like” sample structure was subsequently created (Figure 2). The thermal conductivity $\lambda_{10\text{dry}}$ was determined on the sandwich samples.
3 | RESULTS AND DISCUSSION

Commonly in thermal insulation, porous materials play a significant role. Equation (1) simply describes the equivalent thermal conductivity through porous materials, i.e.,

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\lambda_{\text{insulation}} = \lambda_{\text{solid}} + \lambda_{\text{convection}} + \lambda_{\text{fluid}} + \lambda_{\text{radiation}} \quad \left[ \frac{\text{W}}{\text{m} \cdot \text{K}} \right],
$$

where $\lambda_{\text{insulation}}$ is the apparent thermal conductivity of the insulation material; $\lambda_{\text{solid}}$ is the thermal conduction through the solid parts in the material; $\lambda_{\text{convection}}$ is the macroscopic movement of the gas particles; $\lambda_{\text{fluid}}$ is the gas conduction through the pores; and $\lambda_{\text{radiation}}$ is the heat radiation passing through the material.56

As previously mentioned, heat transfer through the solid components of the highly porous materials contributes only one quarter of the total heat transfer. The lower the bulk density of the materials is the smaller the effect of the solid conductivity in the total heat transfer through an insulator.

3.1 | Morphological study

TEM studies were performed to explore the influence of different solvents and the addition of CB on the size of the nanofibers. Single PS nanofibers were electrospun directly on the TEM grid. Figure 3 shows the TEM images of the three PS samples. The average diameter of the PS-DMF nanofibers stays in the range of 250 to 500 nm. In Figure 3A, one can see that this sample shows differences in darkness intensity. Such differences are initiated by differences in the density of the PS in fibers, probably due to the outer and/or inner porosity.

In contrast to PS-DMF, electrospinning from the DMF-DCM mixture allowed us to increase the ratio of extremely volatile solvents, resulting in the increasing diameter of the fibers from 2.2 to 2.3 $\mu$m in a mixture with DCM (1:3) (Figure 3B). Increased concentration of the fast evaporating solvent increases the rate of solidification, resulting in fiber generation of higher diameters. Similar behavior was studied by Reneker’s team57 by increasing the relative humidity during electrospinning of polyethylene oxide fibers from aqueous solution. Increasing humidity leads to decreasing water evaporation rates, resulting in a significant reduction of the nanofiber diameter.

Embedding the CB in the nanofiber structure leads to a slightly reduced nanofiber diameter (200 to 350 nm, Figure 3C) due to the changes in viscosity and conductivity of the electrospun solution, as well as a charge density on the jet surface.58

In order to confirm the morphology changes, the TEM investigations were correlated with the results from SEM at very low voltage and HIM. Both techniques are extremely sensitive to surface topography and were applied without any surface modification such as sputter coating. SEM images were taken with acceleration voltages of 500 V and below and probe currents of 50 to 100 pA. Thereby, charging effects could be significantly reduced; however, they were not completely suppressed. In the case of HIM, an electron flood gun for charge compensation allows for imaging of nonconductive samples without charging artifacts. For optimal imaging, an acceleration voltage of 30 kV was used, with imaging voltages

![FIGURE 3 Transmission electron microscopy images of the polystyrene (PS) nanofibers: A, PS-DMF; B, PS-(DMF-DCM); C, PS-CB. CB, carbon black; DCM, dichloromethane; DMF, dimethyl formamide](image-url)
of around 36 kV and a probe currents around 0.3 pA. Thus, surface roughness or surface porosity could be thoroughly investigated using SEM and HIM (Figure 4).

The morphology of all samples of the electrospun fibers was influenced by the production conditions, ie, using single- or mixed-solvent systems. Surface topography evolution was found to be similar for PS-DMF and PS-CB. The nanofibers look like as bundles of thin fibers with a distinct roughness. A significantly different trend was observed for PS-(DMF-DCM). When adding DCM as a solvent, the fiber diameter increases, even the similar yarn-like structure is formed. Larger fiber diameter leads to the formation of smooth outer surfaces. These findings suggest that, for all PS samples, the same conclusions can be drawn with respect to influencing factors such as solvent volatility, solvent nature, and the solvent ratio.

### 3.2 Porosity evaluation

The skeletal density of three types of the insulation mats produced by electrospinning of the waste EPS was investigated by helium pycnometry. Both pure PS nanofibermats show a skeletal density of 1.06 g/cm³, whereas the PS-CB sample has a skeletal density of 1.15 g/cm³. The observed values for the pure PS samples (PS-DMF and PS-(DMF-DCM)) are slightly higher than the typical density value reported for PS (1.04 to 1.05 g/cm³). The higher density value of PS in fiber structure may be explained by possible polymer chain stretching and dense packing under the complex force conditions: electric field, charge at the surface, fast solvent evaporation, whipping instability, etc. In the case of the PS-CB sample,
FIGURE 5  Mercury intrusion curves of the different fibrous polystyrene (PS) materials. CB, carbon black; DCM, dichloromethane; DMF, dimethyl formamide

TABLE 1  Extraction of the material properties from mercury intrusion porosimetry (MIP) tests and gas displacement pycnometry (GDP)

| Sample             | Total intrusion volume, ml/g | Bulk density (MIP), g/ml | Skeletal density (MIP), g/ml | Skeletal density (GDP), g/ml | Porosity (MIP), % | Porosity (GDP), % |
|--------------------|-----------------------------|--------------------------|-----------------------------|------------------------------|------------------|------------------|
| PS-DMF             | 6.02                        | 0.13                     | 0.67                        | 1.06                         | 80               | 87               |
| PS-(DMF-DCM)       | 6.54                        | 0.12                     | 0.69                        | 1.06                         | 82               | 88               |
| PS-CB              | 4.13                        | 0.19                     | 0.80                        | 1.15                         | 77               | 84               |

Abbreviations: CB, carbon black; DCM, dichloromethane; DMF, dimethyl formamide; PS, polystyrene.

the observed density is significantly higher than for the two other materials. However, including CB with a density of 2.0 g/cm³ increases the density of the produced material.59

To examine the effectiveness of the electrospun PS materials regarding the gas conductivity, we evaluated the porosity of our tested samples concerning their pores size distribution. Figure 5 shows the mercury intrusion curves of the three PS-sheets. The experiment was performed from 3.5·10⁻³ MPa up to 418 MPa. The total intrusion volume varies from 4.13 ml/g for PS-CB to 6.54 ml/g for PS-(DMF-DCM) (Table 1).

Figure 6 shows the corresponding pore size distribution. All materials show a steep increase in their intrusion behavior right from the beginning of the analysis associated with a broad polymodal pore size distribution. The main part of the pores is in the range of 1 to 300 µm (Figure 6A). Those pores are generated from the interfibrous free spaces. The first step in the intrusion curve is observed at around 0.2 MPa, which is due to transferring the sample cells from a low-pressure to a high-pressure chamber of the measurement set up. Between approximately 0.7 and 2 MPa, we see a second step in the intrusion curves. This is most likely the pressure range at which the filling of the interfiber space is finished. All materials show a pronounced maximum in that region: PS-DMF = 1.8 µm, PS-(DMF-DCM) = 3.4 µm, and PS-CB = 0.98 µm (Figure 6A). The examined sizes are on the scale of the fiber diameters that were observed with the previously discussed imaging analyses. As expected, PS-(DMF-DCM) consisting of larger fibers than the other two materials also shows the largest interfiber pore sizes. The intrusion at pressures higher than 3.4 MPa reflects the filling of pores inside the fibers itself. PS-DMF shows a pronounced peak in the pore size distribution with a maximum of about 90 nm. In comparison, PS-(DMF-DCM) shows a broader distribution in the range of 10 to 200 nm. PS-CB shows the smallest number of pores in that size range with a small maximum at 90 nm. Figure 6B shows the pore size distribution displayed as differential intrusion versus pore size. This method puts a higher emphasis on smaller pore sizes and reveals that the two nanofiber mats produced from pure DMF also have smaller pores with sizes of about 9 nm. The polar solvent DMF with a high boiling point results in slow evaporation and mixing with water, which is absorbed on the jet surface, which leads to generation of nanosized pores.

Results from mercury intrusion porosimetry were also used to calculate the bulk density, skeletal density, and percent porosity of the three types of PS samples. Bulk densities were calculated at the filling pressure of 3.5·10⁻³ MPa and vary from 0.13 to 0.19 g/cm³, whereas the skeletal densities show values between 0.67 and 0.80 g/cm³ and were calculated at the last pressure point (418 MPa). Table 1 summarizes the results obtained from MIP studies. As already observed
with helium pycnometry, PS-CB has a higher density than the two other PS materials. However, comparing the densities derived from MIP with those obtained from helium pycnometry, we see that the helium densities are significantly higher. Such differences are not unusual as MIP is restricted to pore sizes of about 4 nm, meaning that the volume of smaller pores or pores being restricted by smaller necks (eg, in more complex pore networks) will not be subtracted from the material volume. The material porosity obtained from MIP calculations varies from 76 to 82%. If the helium skeletal densities are used to calculate the percent porosity, the values increase to 83 to 88%.

In summary, PS-(DMF-DCM) shows the highest intrusion volume as well as the highest pore sizes and percent porosity. This is the expected behavior, as the material was produced using the solvent mixture (DMF: DCM, 1:3), where fast evaporation of dichloromethane occurred and mixing up of DCM with water is not expected. In this case, the size of the pores on the fiber surface is significantly higher. Embedding CB into the fiber structure, on the other hand, reduces the pore sizes of μm size. This material also shows the lowest intrusion volume and a lower percent porosity than the other two PS samples.

Gas adsorption experiments can give further insight in the material properties. Figure 7A shows the isotherms performed with nitrogen at 77 K. The isotherm shapes are typical for materials showing mainly larger mesopores and macropores. Comparison of the three isotherms shows that PS-CB has the smallest uptake of adsorbed gas, which is in good agreement with the results obtained from MIP. Performing several adsorption experiments on the same materials shows that the fiber samples are not very homogeneous, as BET areas varied between 38 and 44 m²/g for PS-DMF, between 59 and 61 m²/g for PS-(DMF-DCM), and between 13 and 17 m²/g for PS-CB. However, a clear trend is maintained, which is also reflected in the BJH pore size distribution (Figure 7B). PS-DMF and PS-(DMF-DCM) both show a significant
number of pores between 10 and 100 nm, whereas PS-CB shows only a minor number of pores at all. Some extent of pores having sizes smaller than 10 nm can be observed for PS-DMF and PS-CB. Those results are in good agreement with the material properties observed in mercury intrusion porosimetry.

### 3.3 Heat transfer

To highlight the advantage of the fibrous morphology of electrospun waste-PS materials for applications such as building insulation, we investigated their thermal transport properties as freestanding materials and in the sandwich structures between different building materials. Several experimental techniques have been used to evaluate the thermal conductivity in insulation materials.\(^{60,61}\) However, evaluation of the insulation potential in the electrospun nanofiber sheets is a great challenge, due to their sensitivity to pressure, which modifies the porosity and packaging nanofibers in the material. In general, researchers mainly focus on the thermal conductivity measurements along the individual fiber length, showing extremely high thermal conductivity when compared to bulk materials.\(^{62}\) In our early study, we have also found high anisotropy in the thermal conductivity of the electrospun thin membranes: These materials are highly conductive in the plane direction but with extreme insulation behavior perpendicular to the plane.\(^{63}\) The transient plane source technique, which is a basis of the hot disk method, is one of the most acceptable methods for the measurement of polymer nanofiber-based materials. The main advantage of the hot disk method is the elimination of the contact resistance effect in the analysis. Thus, it does not require specific surface preparation, a step that is undesirable for the materials. The excellent insulation behavior is confirmed for PS-DMF, PS-(DMF-DCM), PS-CB materials, and PS-MWNT (Figure 8). The differences between the samples were insignificant.

During the hot disk measurements, the dependence on a pressure applied to the sample was investigated. The measurements showed a significant increase of the thermal conductivity at the stage of the application of low pressure. The

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**FIGURE 7** Nitrogen Sorption Isotherms performed at 77 K (A) and BJH pore size distribution (B) of the three polystyrene (PS) samples. Closed symbols show the adsorption, whereas open symbols represent the desorption. CB, carbon black; DCM, dichloromethane; DMF, dimethyl formamide
volume of pores is dramatically modified as the sample changes from a freestanding material to a compressed one. After saturation of the compressed pore volume, the thermal conductivity reaches saturation also and the values do not change significantly thereafter. It can be assumed that, at a pressure of around 0.01 kg/cm², the thermal conductivity threshold in the compressed nanofiber materials is observed. The measurement of the free-standing nanofiber-sheets, where the volume of the gas molecules is not modified in the sample, showed the lowest conductivity of the samples (20 mW/mK) with the lowest porosity in the PS-(DMF-DCM) sample (Figure 8, brown). This is in good correlation with the porosity results (Table 1). The decrease of the porosity leads to increasing the thermal conductivity for the PS-DMF sample (24 mW/mK). This difference can be explained by increasing the quantity of the polymer in the sample, which is more conductive compared to air (200 and 24 mW/mK, respectively). For the PS-CB sample, thermal conductivity was found 23 mW/mK. Lower porosity of the PS-CB sample (77%, (Table 1)) was compensated by the blackness of the nanofiber sheets, which reduces the effect of the IR conductivity. This tendency was confirmed by the additional black sample (thermal conductivity 23 mW/mK), where 60% of the CB was substituted with MWNTs. Another behavior was observed by testing compressed samples. The sample with the highest porosity (PS-(DMF-DCM)) showed the highest thermal conductivity under a pressure of 0.12 kg/cm² (34 mW/mK). The reduced value (32 mW/mK) for the PS-DMF sample is detected due to the higher amount of the small pores on the nanofiber surface (Figure 6B). In the compressed samples, the effect of the interfiber pores (pores between fibers) is reduced by compression. The small inner pores and the pores on the fiber surface play a more significant role in the thermal conductivity of the produced samples. Additional decreases in the thermal conductivity of the compressed samples may be explained by the decreasing effect of the IR heat, where IR radiation is absorbed by the black carbon particles present in the nanofiber structure. Increasing the concentration of the black particles further reduces the thermal conductivity of the compressed nanofiber sheets. From the results, we conclude that, in the nanomaterials, the size and number of the nanosized pores are more important for the insulation properties of the materials than its total porosity. Including the black bodies in the nanofiber structure reduces the effects of the IR radiation on the insulation properties of the nanosized insulation materials.

One of the main purposes of our research is the application of the electrospun waste-PS in building insulation materials. In this study, the materials were tested in combination with different materials, which are used in the building industry: lime sandstone, geopolymer, thin-bed mortar, bricks, thermal insulation plaster, aerated concrete, and foamed geopolymer.

The 1 mm-thick sheets of the electrospun PS-DMF, as the most promising material, were sandwiched between two blocks of each building materials in one, two, and three layers. The thermal conductivity was evaluated and was compared with the nanofiber free materials. The results are summarized in Figure 9.

The combination of the conventional building with the nanosized insulation materials is a well-known approach. For example, 50% volume of aerogel embedded into the mortar reduced its thermal conductivity by factor 5. The thermal conductivity of the materials based on the conventional and high-performance building materials and waste PS nanofiber sheets decreased in the sandwich structures. Application of only a 1 mm layer of the nanofiber sheet (around 5% volume from the volume of the tested sandwich) leads to the enhancement of the insulation properties from 15% for aerated...
Thermal conductivities of sandwich samples of different building materials with increasing layer thickness of the inserted nanofiber mats compared to the reference samples concrete to 61% for the lime sandstone. A strong decrease in thermal conductivity of the conventional building materials with small amount of the nanofiber sheets allows us to suggest that materials have great potential for the restoration of the historic buildings in the narrow parts of the old towns. Insulation of such buildings can be made without modifying the wall thickness. Thin (1 mm) layer of the PS-nanofiber sheet can be adhered to the existing wall and covered with a thin layer of the conventional building material, making a sandwich similar to the one described here. According to PS hydrophobicity (contact angle of the water drop deposited on the PS-nanofiber sheet surface was measured as high as 87°) and to the literature results, we also expect that moisture adsorption in the pores will not be higher than found for expanded PS boards (3.2%, for 28 days of immersion). PS is an inert polymer, which is stable to microorganisms. We expect no effect of thin PS-nanofiber sheet layer on the ancient building materials. An increase in the nanofiber layer thickness up to 3 mm allowed us to produce building blocks with a thermal conductivity ranging from 0.103 W/mK for aerated concrete to 0.189 W/mK for the lime sandstone sample. The thermal conductivity of the tested samples is in the range of the performance of the hydraulic lime or Saint Astier plasters enhanced with 25% volume of aerogel. Sandwiching of the PS-nanofiber-sheets is a simple universal method, which can be applied to any building material systems with relative high efficiency. Sandwiching of the insulation waste-PS-nanofiber sheets between two slabs of building materials allowed us to break the direct heat passage through the building material sample, distributing the heat along the nanofiber direction due to the high anisotropy (Figure 10). The thermal conductivity of the two brick slabs of our study was measured to be as high as 0.3 W/mK, which is higher than with nanofiber insulation sheets. This is explained by nanosized barrier generated by the inner-fiber pores that are present in the fiber structure (Figures 4 and 6). Due to the Knudsen Effect, which occurs if the mean free path of the gas molecules is larger than the pore diameter, the thermal conductivity of the sandwich materials reduced significantly. The mean free pass of air molecules ranges from 63 to 68 nm, depending on temperature and humidity. This is indeed much larger than the inner-fiber pores size is measured as 9 nm. The obtained thermal conductivity data is in good correlation with the hot-disk measurements, where three layers of nanofiber sandwiches showed 0.122 and 0.146 W/mK conductivity for the thin-bed mortar and for brick samples, respectively.
CONCLUSIONS

In this work, high-performance nanofiber-based building insulation materials from EPS, recovered from building sector, are easily produced by means of electrospinning. The surface and interfiber porosity is controlled by mixing solvent concentrations. The manufactured nanofiber sheets are macroscopically homogeneous and show the excellent insulation properties, eg, very low thermal conductivity. The porosity and morphology of the nanofiber sheets are evaluated by mercury porosimetry, BET measurements, TEM, SEM, and HIM. Application of the nanofiber insulation sheets in the sandwich structures with a variety of building materials shows significant enhancement of the insulation potential of the building constructions. Thus, the manufacturing provides a simple method of fabrication of smart nanofiber sheets for a wide range of technical applications as freestanding building insulation materials and/or in combination with conventional building materials from waste EPS.

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ORCID

Vitaliy Datsyuk https://orcid.org/0000-0001-5137-190X

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