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Phenyl-methyl phosphazene derivatives for preparation and modification of hydrophobic properties of polymeric nonwoven textiles

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ABSTRACT

This paper focuses on the preparation of two types of hydrophobic nanolayers using electrospinning technology. The first synthetic approach consists in direct fiberizing of polymeric phenyl-methyl-polyphosphazene Ph-Me(p) with the aim to preparing nanolayers that have significant hydrophobicity and thermal stability. The preparation of Ph-Me(p) is a multi-step reaction which produces a relatively low amount of the product. The second area of our interest was the creation of nanofibers formed from a mixture of some commercially available organic polymers and a *cyclo*-phosphazene derivative. In this case, tri(phenyl)-trimethyl-*cyclo*-triphosphazene, Ph-Me(t), whose synthesis is less complicated than its polymeric form, was used as an additive. The influence of the Ph-Me(t) additive in the nanofibers on the affinity to water was compared with the affinity of nanolayers made from a pure commercial polymer, i.e. without any phosphazene additive. It was also shown that the hydrophobic properties of fibers formed from Ph-Me(p) dissolved especially in THF are better than those of the nanofibers composed of a commercial polymer with the addition of Ph-Me(t).

1. Introduction

There are many researchers who concentrate on the functionalization of nanofiber layers. However, this modifying process, influenced by the structure of the respective polymer, leads to newly created bonds that could modify significantly the properties of the final product [1]. It is usually expected that any additive to a polymer can preserve the polymer's original chemical structure wherein certain physical properties (such as hydrophobicity) of the modified polymer can be changed. [2].

It can be also expected that the original properties of a polymer and those of the additive merge into more suitable properties of the resulting material. A common *cyclo*-phosphazene derivative, containing non-polar organic side groups, could significantly increase the hydrophobic character of the whole *cyclo*-phosphazene molecule [10] as well as the hydrophobic character of the whole modified polymer. The mixture, containing a polymer and an additive, can be further shaped by various processing techniques, e.g. electrospinning, which is widely used for producing polymer nanofibers.

The following phosphazene compounds – trimeric tri(phenyl)-trimethyl-*cyclo*-triphosphazene, Ph-Me(t) (used as an additive), and polymeric phenyl-methyl-polyphosphazene, Ph-Me(p) – were synthesized according to the methods proposed by Patty Wisian-Neilson [3,4] (Schemes 1 and 2).

The electrospinning technology, which was used in the fiberizing process, is based on the creation of fibers in a high electrostatic field. The nanofibers are created from the surface of a polymer solution (or from its melt) placed on the top of the static powered rod. When the electrical field reaches its critical value, nanofibers are ejected from the positively-charged rod electrode towards the grounded negative electrode, called the collector. The solvent evaporates during this process and nanofibers are deposited on the supporting textile material, e.g. polypropylene foil (PP band), that the collector is covered with. [5–9] Fig.1 shows the scheme of the electrospinning device.

Nanotextiles, made commonly by electrospinning from commercial polymers, can be modified either by addition of the simple phosphazene Ph-Me(t), or they can be made directly from its polymeric form, i.e. Ph-Me(p). The polymeric nanolayers should exhibit, due to a higher number of organic –CH, –CF_3 groups and thin fibers, a relatively high hydrophobicity.

Abbreviations: Ph-Me(t), tri(phenyl)-trimethyl-*cyclo*-triphosphazene; Ph-Me(p), phenyl-methyl-polyphosphazene; PA6, polyamide 6; PS, polystyrene; ASA, acrylonitrile-styrene-acrylate; SAN, styrene- acrylonitrile; PESU, polyethersulphone; PP, polypropylene; THF, tetrahydrofurane; TFA, trifluoroacetic acid; DMS, dimethyl sulfide; AFA, mixture of acetic and formic acids; T_d^a, minimum thermal decomposition temperature; TGA, thermogravimetric analysis; SEE-system, Surface Energy Evalution system analysis; SEM, scanning electron microscope; EDX, X-ray photo-electron spectroscopy; ATR-FTIR, attenuated total reflectance Fourier transform infra-red; NMR, nuclear magnetic resonance.

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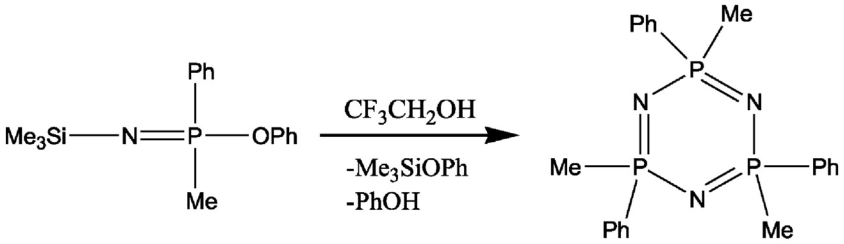
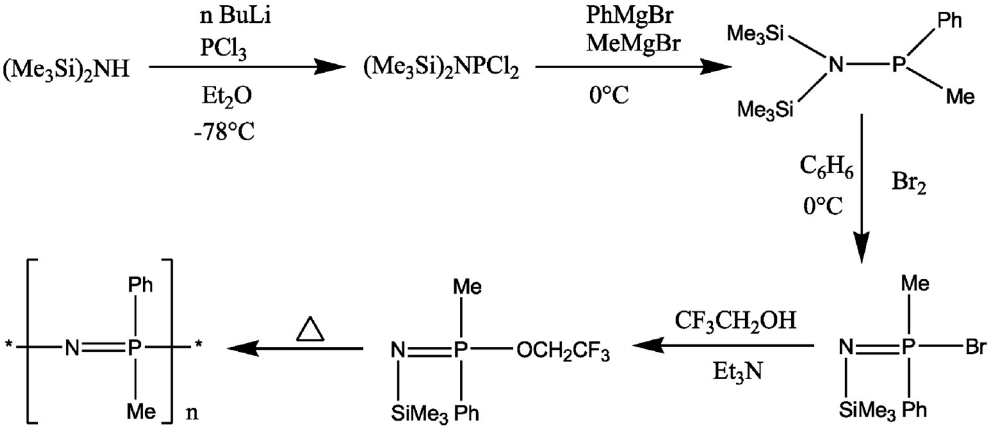


(Ph-Me(t))

Scheme 1. Synthesis of Ph-Me(t).



(Ph-Me(p))

Scheme 2. Synthesis of Ph-Me(p).

The resulting nanolayers can be manually removed from the supporting textile and used, e.g. as a protective material.

2. Experimental

2.1. The preparation of solution for electrospinning

Nanofibers were made from two different solutions, which differ in their composition.

- The commercial polymers – Polystyrene (PS), Polyamide 6 (PA6) or Polyethersulphone (PESU) – or copolymers – acrylonitrile-styrene-acrylate (ASA) or styrene-acrylonitrile (SAN) – were fiberized on their own (Fibers 1) and with Ph-Me(t) as an additive (Fibers 2).
- Ph-Me(p) was fiberized on its own (Fibers 3).

The properties of all the resulting types of nanofibers were compared with each other.

2.1.1. Solutions of commercial organic polymers with and without Ph-Me(t) as additive (Fibers 1, 2) and creation nanofibers from these solutions

The commercial polymers (PA6, PS, ASA, SAN, PESU) were produced by BASF, the solvents were delivered by Sigma Aldrich.

The above mentioned polymers were first dissolved in one of the following diluents — trifluoroacetic acid (TFA), a mixture of acetic and formic acids (AFA) or dimethylformamide (DMF). The prepared solutions of polymers were, for the following experiments, divided into two parts. The first part of the samples was fiberized on its own, i.e. nanofibers were created only from a single polymer or copolymer (Fibers 1). The second part of the samples was mixed with Ph-Me(t) (as an additive) (see Table 1). The content of Ph-Me(t) was either one or ten weight per cent related to the whole commercial polymer contained in the fiberized mixture. It follows from preliminary experiments that a 10 wt.% concentration of Ph-Me(t) is optimal for sufficient modification of fibers (Table 1). Therefore, more space in this article is devoted to fibers containing ten weight per cent of the Ph-Me(t) additive in the fiberized mixture.

The solutions were manually homogenized for 1 h using an electromagnetic stirrer before electrospinning.

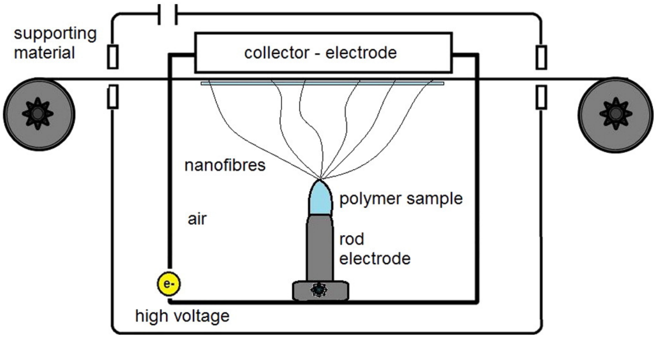


Fig. 1. Scheme of the electrospinning apparatus.

Table 1
The composition of fiberizing solution and electrospinning characteristic.

Polymer	Solvent	Concentration ratios (wt.%)		
		Ph-Me(t)	Organic polymer	Solvent
PA6	TFA, AFA	1.19	11.86	86.96
PS	DMF	2.44	24.39	73.17
ASA	DMF	2.44	24.39	73.17
SAN	DMF	2.44	24.39	73.17
PESU	DMF	1.96	19.61	78.43
Ph-Me(p)	THF, TFA	without	25.0	75.0

Nanofibers were formed from the powered rod electrode (see Fig. 1) using the Elmarco Nanospider™ NSLAB 500 pilot plant unit. Polypropylene foil (PP foil) was used as the supporting material covering the grounded electrode. In the electrospinning process, drops of the polymer solutions were placed on the top of the electrode rod, while all the drops were approximately the same size. Each drop was later fiberized for at least 5 min. To create an approximately 50-μm-thick nanolayer, the deposition process had to be repeated five times. Then, nanofibers were removed from Nanospider together with the supporting PP foil and were allowed to dry at 25 °C for 1 h in order for the rest of the solvent to evaporate. Then the samples were placed in plastic bags for further analysis.

The composition of the polymer solutions used is shown in Table 1. The parameters, such as electrode distance, voltage and current, were kept at approximately the same level for all samples. The distance between electrodes was 170 mm, the voltage was 40 kV and the current was around 0.003 mA.

2.1.2. Solution of Ph-Me(p) (Fibers 3)

The solution of Ph-Me(p) in a 25 wt.% concentration was prepared in THF or TFA (see Table 1). This solution served as a source for creating nanofibers.

2.2. Nanolayer analysis

The chemical composition of nanofibers was determined by physicochemical methods. The presence of the phosphazene additive, Ph-Me(t), in the fiber layers was confirmed by the ATR-FTIR and ^{31}P NMR spectroscopies. The elemental composition of fibers, made from Ph-Me(p), was confirmed by the EDX, ATR-FTIR analyses and also by ^{31}P NMR spectroscopy. The macroscopic structure of the fibers was investigated using the SEM technology and their hydrophobicity was determined using the SEE system analysis. The thermal stability of nanofibers was investigated by TGA analysis.

2.2.1. ATR-FTIR analysis

Attenuated total reflectance Fourier transform infra-red spectra (ATR-FTIR) were measured by the Brucker Vertex 80 V spectrometer. The solid samples were measured in attenuation total reflection mode using a diamond crystal. The sample compartment was evacuated to 2.51 hPa. The spectral range was calibrated from 4000 to 600 cm^{-1}. Each spectrum was scanned a hundred times. Bruker OPUS software was used for spectra evaluation and the baseline correction was done by "rubber-band".

The characteristic vibration of the phosphazene cycles was observed about at 1210 cm^{-1} [10].

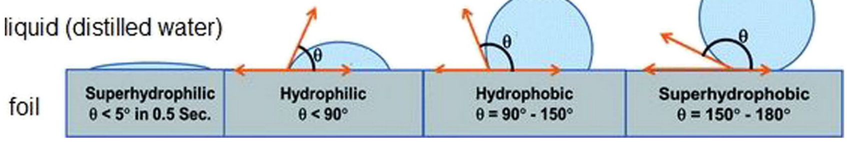


Fig. 2. The contact angle for hydrophilic and hydrophobic materials.

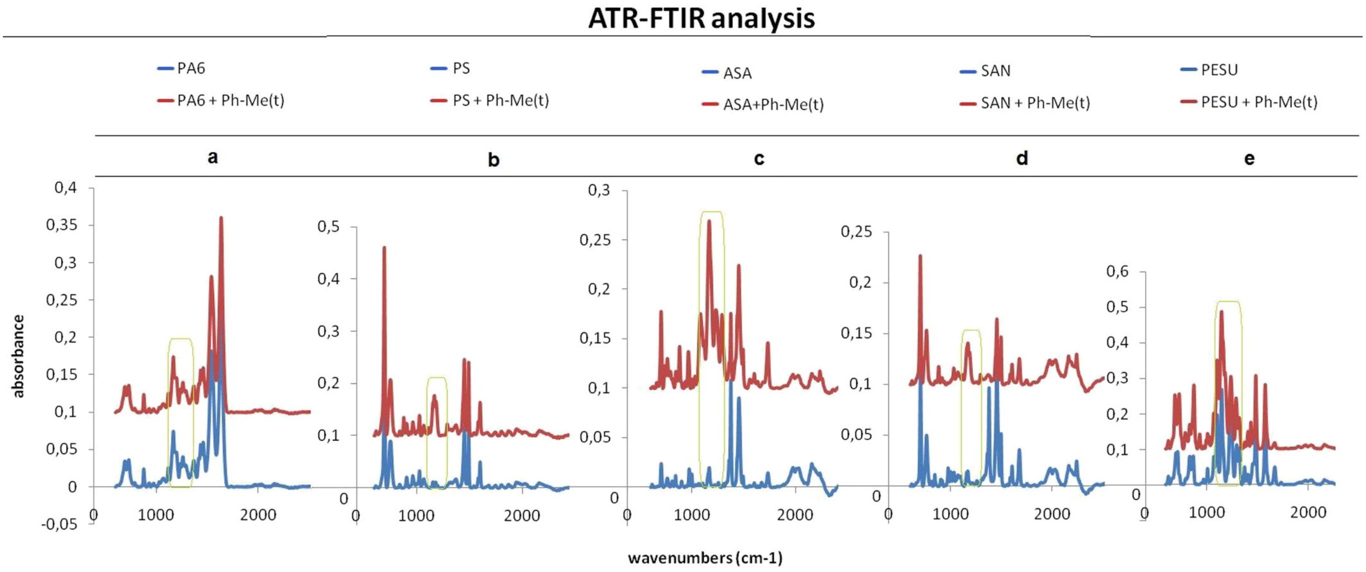


Fig. 3. a–e: ATR-FTIR spectra of fibers made from commercial polymers and those made from commercial polymers with Ph-Me(t) as an additive.

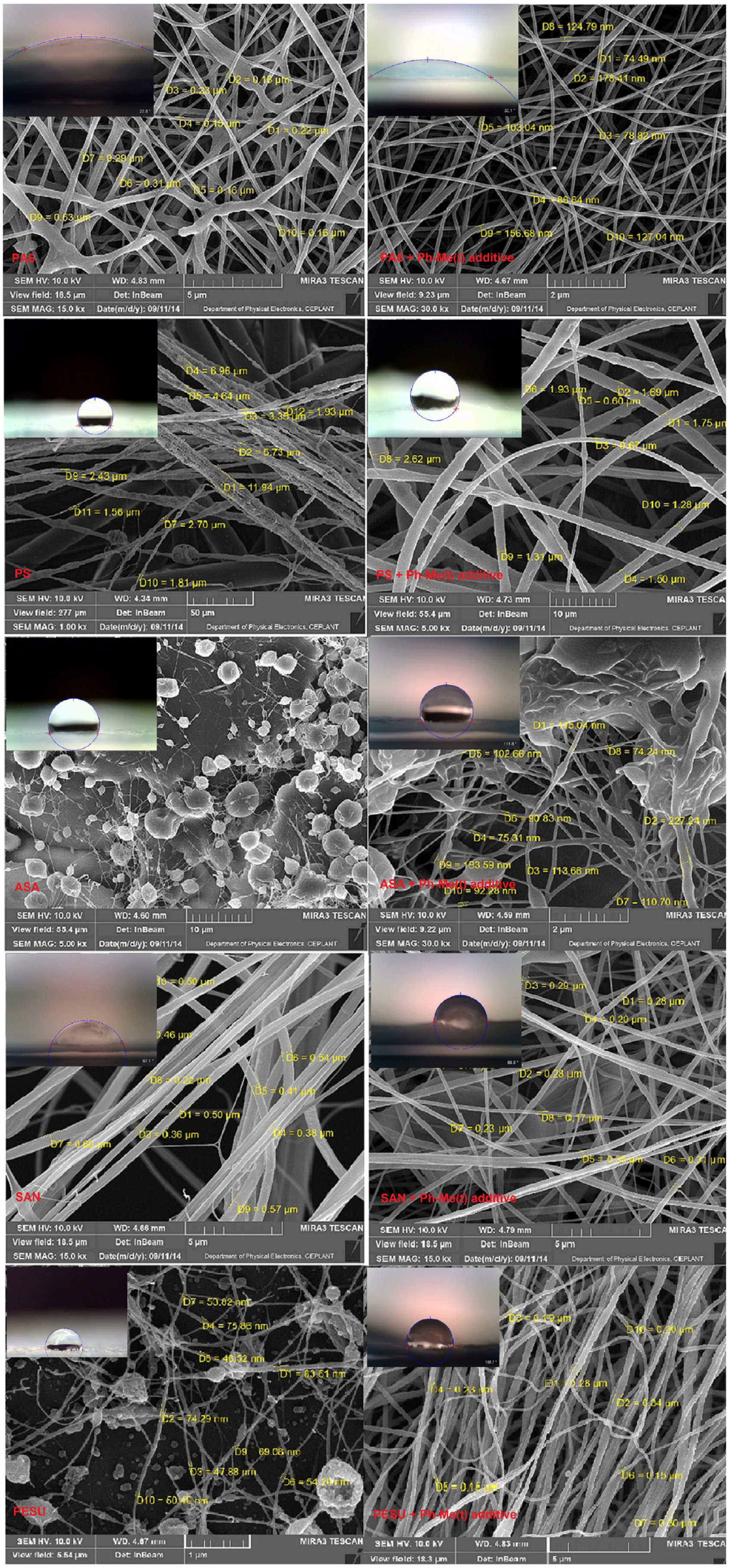


Fig. 4. The SEM nanofibers structures and water drops on the nanofibers.

2.2.2. ^{31}P NMR spectroscopy

^{31}P NMR spectra were measured in solutions of dissolved nanotextile. The spectra were recorded using a BRUKER AVANCE DRX 300 instrument at the frequency of 202.46 MHz, 85% solution of H_3PO_4 was used as the external standard. The samples were sealed in Simax tubes (4 mm in diameter), inserted in NMR cuvettes (5 mm in diameter) filled with D_2O (external lock). The spectra were measured in the coaxial NMR cuvette system.

2.2.3. SEM analysis with EDX detector

The images of the nanofibers were made using the Tescan MIRA3 scanning electron microscope (SEM) equipped with energy X-ray dispersive (EDX) analyzer. The nanolayer was fitted onto the pad using a sticky tape and its surface was covered by a 30 nm gold layer. The samples were measured using the secondary emission mode, the depth regime of 15 kV, the working distance (WD) of 10 mm and 20,000× magnification. Contrast-enhancing coloring was used for contrast visualization. The fiber size was determined using ImageJ software with manually located fiber borders. [11] The surface elemental analysis was determined by Energy Dispersive X-ray Spectroscopy (EDX) (Oxford Instruments) and evaluated by Aztec 2.1a software.

2.2.4. Surface energy evaluation system analysis (SEE system analysis)

The contact angle between the free surface of nanolayers and the water drop characterizes the extent of hydrophobicity. [12] Constant volumes of distilled water were dropped on the nanolayer surface lying on the microscope pad. Photos of water drops were made, the contact places between the drop and the supporting textile were manually marked and the contact angle was determined (Fig. 2).

The SEE system results were evaluated using Software 7.0.

2.2.5. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was carried out using a TA Instruments TGA Q500. The samples of nanofibers, about 1.350 mg, were investigated at heating rate 10.0 °C/min, in the temperature range 20–1000.0 °C. The air was used as a purge gas at the flow rate of 60.0 ml/min. The minimum thermal decomposition temperature (T_d^a) was determined.

3. Results and discussion

Three types of nanofibers were prepared:

- Fibers made from additiveless polymer/copolymer (Fibers 1) and fibers made from polymer/copolymer with Ph-Me(t) as additive (Fibers 2) (see Chapter 3.1.).
- Fibers made from Ph-Me(p) (Fibers 3) (see Chapter 3.2).

3.1. Fibers made from organic polymer/copolymer with and without Ph-Me(t) as an additive (Fibers 1, 2)

ATR-FTIR analysis was performed for both types of nanofibers (Fig. 3).

Table 2
The contact angle value depending on the amount of additive Ph-Me(t).

wt.% of Ph-Me(t)in fibers		0	1	10
Polymer/copolymer	Contact angle (°)			
	PA6	22.7	23.5	31.3
	PS	119.9	120.1	122.9
	ASA	110.3	111.2	112.7
	SAN	68.3	70.4	89.7
	PESU	93.0	93.8	97.1

In the spectra of fibers containing Ph-Me(t) and PS, ASA and SAN (Fig. 3b, c, d), vibrations at around 1200 cm^{-1}, belonging to the phosphazene cycle, were observed while no vibrations at about the same wavenumber were found in the pure polymer spectra. In the case of PA6 and PESU, it was difficult to determine Ph-Me(t) vibrations (Fig. 3a, e), because the vibrations at around 1200 $cm^{-1,}$ belonging to Ph-Me(t), overlapped with those of the pure polymers.

To avoid these problems with the identification of bands, the presence of Ph-Me(t) in the nanofibers had to be confirmed by another method, e.g. ^{31}P NMR analysis. The nanolayer, prepared from Ph-Me(t) and a commercial polymer/copolymer, was peeled from the PP supporting foil, dissolved in THF or TFA and measured. The ^{31}P chemical shift of the Ph-Me(t) extracted from the nanolayer was observed as a singlet at around 18.8 ppm in the spectra. This is in agreement with the value of chemical shift for Ph-Me(t) ($\delta = 19.0$ ppm) synthesized by standard methods [13]. A small split in the signal can be ascribed to the influence of hydrogen atoms from the Ph and Me groups.

The microscopic structure of the nanofiber layers was studied using the SEM technique (Fig. 4).

It follows from the SEM snaps that fibers formed from the PA6, PS and SAN matrix materials are spread relatively homogenously, with just a few irregularities. No fiber orientation is observed there. The fibers made from ASA and PESU do not create homogenous layers. It follows from Fig. 4 that the ASA and PESU samples show the possibility of combination of electrospinning and electrospraying (i.e. the creation of drops instead of fibers). In this case, these drops create centers for further formation of shorter daughter-fibers. These daughter-fibers are relatively thin and inhomogeneous.

The behavior of water drops, being in contact with a nanolayer surface, was tested using the SEE system analysis (the water drops on the nanolayer surface are depicted as small pictures in the corners of Fig. 4 for each sample separately).

Table 2 lists the values of the contact angles for fibers containing only polymers/copolymers (i.e. 0 wt.% of the Ph-Me(t) additive) and polymers/copolymers with the Ph-Me(t) additive (1 wt.% and 10 wt.%).

The influence of the presence of Ph-Me(t) on the average fiber width was also investigated. The individual values of fiber width and the values of contact angles are shown in Table 2.

The increase (↑)/decrease (↓) of the fiber width (mentioned as how many times bigger/smaller the fiber width is) comparing the fibers containing only commercial polymer (Fibers 1) with fibers containing polymer and 10 wt.% of Ph-Me(t) (Fibers 2) is listed in Table 3.

Table 3
The comparison of the value of contact angle and fiber width for 10 wt.% concentration of Ph-Me(t).

Fiber composition and characteristics		
Fiber composition	Mean fiber width value	Average contact angle
PA6	0.25 nm	22.7°
PA6 + Ph-Me(t)	0.11 μm	31.3°
*	↑440×	37.88%
PS	4.19 μm	119.9°
PS + Ph-Me(t)	1.44 μm	122.9°
*	↓2.91×	2.50%
ASA	0.61 μm	110.3°
ASA + Ph-Me(t)	118.55 nm	112.7°
*	↓5.16×	2.18%
SAN	0.45 μm	68.3°
SAN + Ph-Me(t)	0.06 μm	89.7°
*	↓7.50×	31.33%
PESU	60.25 nm	93.0°
PESU + Ph-Me(t)	0.22 μm	97.1°
*	↑3.65×	4.41%

* The increase (↑)/decrease (↓) of the fiber width the percentage increase of the contact angle values.

It follows from Table 3 that the values of contact angles for nanolayers made from PA6 (22.7°) and PA6 with Ph-Me(t) (31.3°), SAN (68.3°) and SAN with Ph-Me(t) (89.7°) show slightly hydrophilic properties, while the contact angles for nanolayers made from PS (119.9°) and PS with Ph-Me(t) (122.9°), PESU (93.0°) and PESU with Ph-Me(t) (97.1°), ASA (110.3°) and ASA with Ph-Me(t) (112.7°) show slightly hydrophobic character.

3.2. Fibers made from Ph-Me(p) (Fiber 3)

A similar electrospinning experiment was also carried out with pure Ph-Me(p). The elemental composition of the resulting polyphosphazene nanofiber layer was also determined by EDX analysis (Figs. 5, 6A, B). The ATR-FTIR spectroscopy (Fig. 7) was used for determination Ph-Me(p) in the nanolayer.

Fig. 5 shows that the distribution of elements contained in Ph-Me(p) follows the structure of the nanofiber layer. The elemental composition of fibers is distinguished in the figure by different colors of elements.

The presence of these elements was also confirmed by the EDX analysis (Fig. 6A, B). The presence of fluorine and oxygen (Fig. 6B) can be explained by using fluorinated solvents (TFA) in the course of fiberizing.

It can be easily concluded from above mentioned results that the fibers are composed only from Ph-Me(p) with residues of solvent.

ATR-FTIR spectra of nanofibers formed from Ph-Me(p) were compared with non-fiberized Ph-Me(p) (Fig. 7). It follows from this figure that the ATR-FTIR spectra of both compared samples are identical. Therefore, it can be concluded that this nanolayer is made only from Ph-Me(p) (with traces of the solvent, which were not evaporated completely, respectively).

The presence of phosphorus in Ph-Me(p) nanolayers was also confirmed using ^{31}P NMR analysis — for polymeric structures typically a broad signal around the base line with a chemical shift of 1.1 ppm (Fig. 8) [13].

The appearance of nanofibers is shown by SEM spectroscopy (Fig. 9). The fiber structure of nanolayers, prepared from THF, is homogenous, while fibers spun from TFA look a little etched (see the red circles in Fig. 9). Individual fibers are not distinguishable there.

The interaction between the nanolayer and water drops was also studied. Both nanolayers (formed from different solvents) have hydrophobic properties as follows from the contact angle values (Fig. 10). Fibers created from THF are a little bit more hydrophobic (124.1°) than fibers spun from TFA (114.2°). The width of Ph-Me(p) fibers created from THF is 1.38 μm and the width of fibers created from TFA is 0.94 μm.

3.3. Discussion of hydrophobicity

It follows from the above mentioned results that the formation of nanofibers from different commercial polymers (PA6, PS, ASA, SAN, PESU) modified by Ph-Me(t) is possible. The same conclusion can be claimed also for nanofibers made from polymeric Ph-Me(p) itself.

Fibrous materials themselves exhibit low wettability in comparison with the same property of a smooth surface of compact pure polymer matrix. It was found that the increased content of Ph-Me(t) in the commercial polymeric fibers (10%) leads to higher hydrophobicity of nanolayers. Generally, the presence of Ph-Me(t) improves unambiguously the final

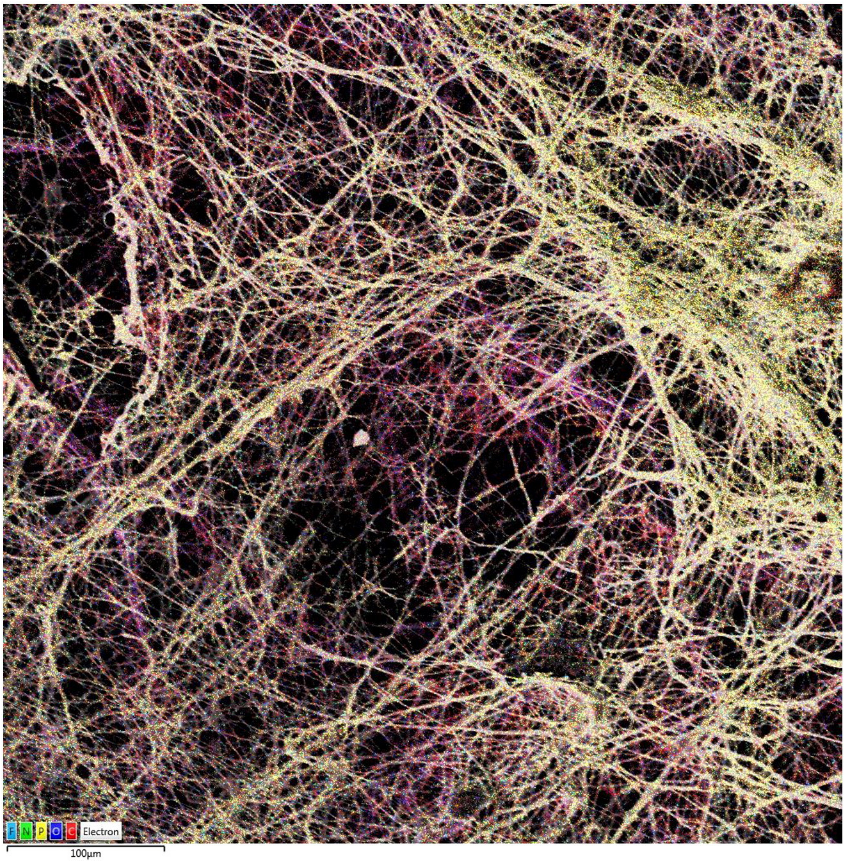


Fig. 5. EDX analysis, (nitrogen — green, phosphorus — yellow, carbon — red, and fluorine — light blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

hydrophobic properties of the whole nonwoven material. This also corresponds to the fact that surfaces created from extremely thin fibers exhibit better hydrophobicity. The comparison of the values of contact angles for commercial polymers with and without Ph-Me(t) is shown in Fig. 11.

With respect to the values of contact angles, we can divide commercial polymers into two basic groups — hydrophilic polymers (PA6, SAN) and hydrophobic ones (PS, ASA, PESU).

Ph-Me(t), as an additive, leads to the increase of hydrophobic properties of originally hydrophilic polymers (PA6, SAN) by about thirty

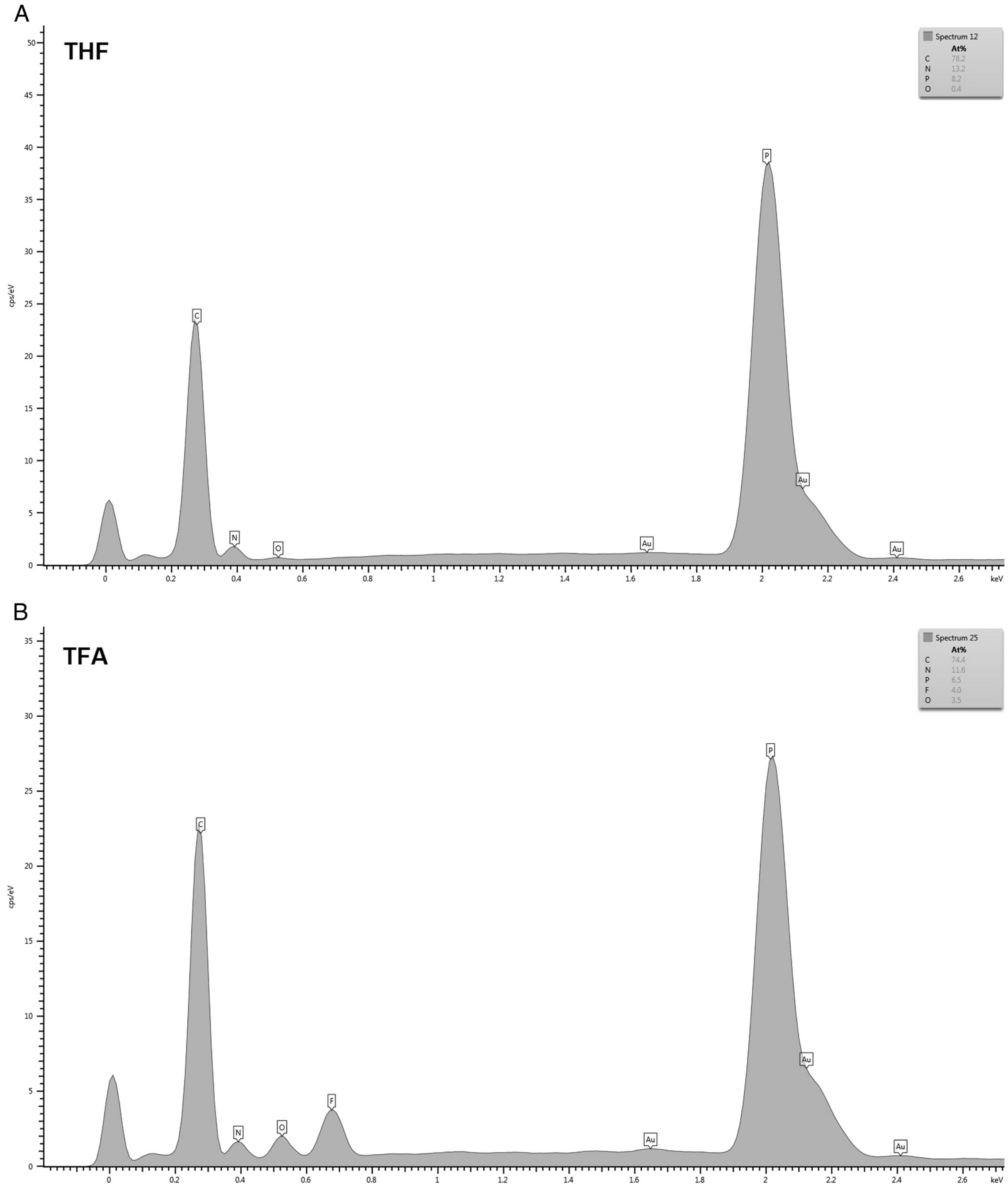


Fig. 6. A: EDX diagrams of Ph-Me(p) nanolayers created from THF B: EDX diagrams of Ph-Me(p) nanolayers created from TFA.

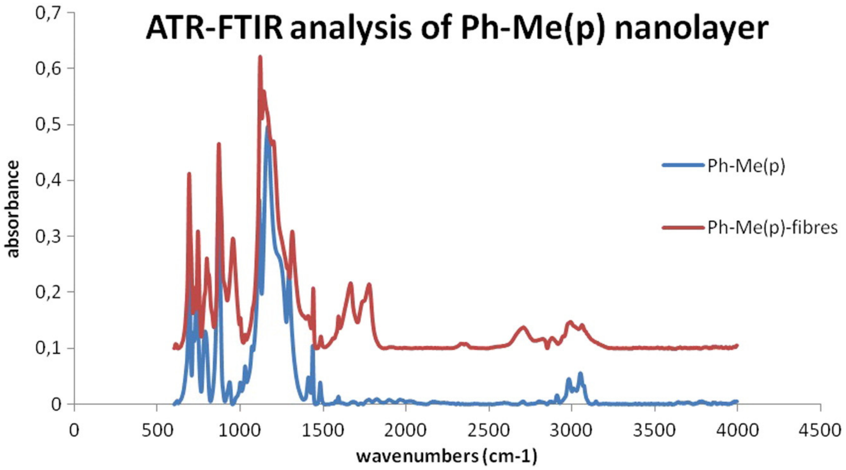


Fig. 7. ATR-FTIR analysis of Ph-Me(p) nanolayer.

percent in contrast to hydrophobic polymers (PS, ASA). Their hydrophobicity grows by only about two percent and for PESU polymer around 4%. The above mentioned results also show the significant influence of the original hydrophobicity of a commercial polymer on the final behavior of the prepared nanolayers. A change in contact angles is more significant for fibers made from more hydrophilic polymers (i.e. from PA6, SAN).

The experiments studying hydrophobicity and homogeneity were carried out using a pure Ph-Me(p) nanolayer, too. Although the size of the nanofibers created from THF is greater, they are more separated and they are spread homogenously without any irregularities, in contrast with nanofibers created from TFA, which are thinner and not so homogeneous due to etched places. This is probably caused by a higher residual amount of TFA in these fiber areas.

The Ph-Me(p) nanolayer has higher hydrophobicity than layers created from commercial polymers with Ph-Me(t) as an additive. The wettability of nanolayer created from Ph-Me(p) dissolved in THF is worse than the wettability of layer from Ph-Me(p) and TFA.

3.4. Thermal stability of the Ph-Me(t) additive in comparison with Ph-Me(p)

It is well known that relatively high content of phosphorus and nitrogen in material leads to the increasing thermal stability [14]. Phosphazene compounds, containing PN groups in the backbone, have been studied for their thermal stability many times [14,15]. Therefore, the TGA analysis was carried out to determine the thermal properties of nanofibers.

The minimum thermal decomposition temperature (T_d^a) of polymeric Ph-Me(p) as well as trimer Ph-Me(t) was determined from TGA curves (see Figs. 12, 13).

The results of TGA analysis confirmed that polymeric Ph-Me(p) ($T_d^a = 230$ °C) decompose at higher temperature than trimer Ph-Me(t) ($T_d^a = 113{,}9$ °C). This result is rather surprising because the ratio of P:N in both substances is equal. That means there must be another reason for this difference. The possible explanation could be in the different structure of phosphazene backbone (cyclic trimer vs. linear polymer). It is highly probable that the thermal decomposition of Ph-Me(t), with relatively high tension of the cycle, is based on the disintegration of the cycle leading to short linear fragments with reactive centers, while almost no similar tension of linear polymeric Ph-Me(p) can be expected. Therefore the thermal decomposition of Ph-Me(p) occurs at a higher temperature as compared with Ph-Me(t).

Further experiments, in which the influence of Ph-Me(t) as the additive onto organic polymers/copolymers was studied, were carried out. T_d^a values, determined for nanofibers containing only commercial polymer/copolymer (Fibers 1) and for nanofibers with content of Ph-Me(t) (Fibers 2) are different (see Table 4).

The results in Table 4 show that T_d^a is significantly decreasing in case of PA6, ASA, PESU while in case of PS and SAN the difference is practically negligible. The explanation of this observation can be based

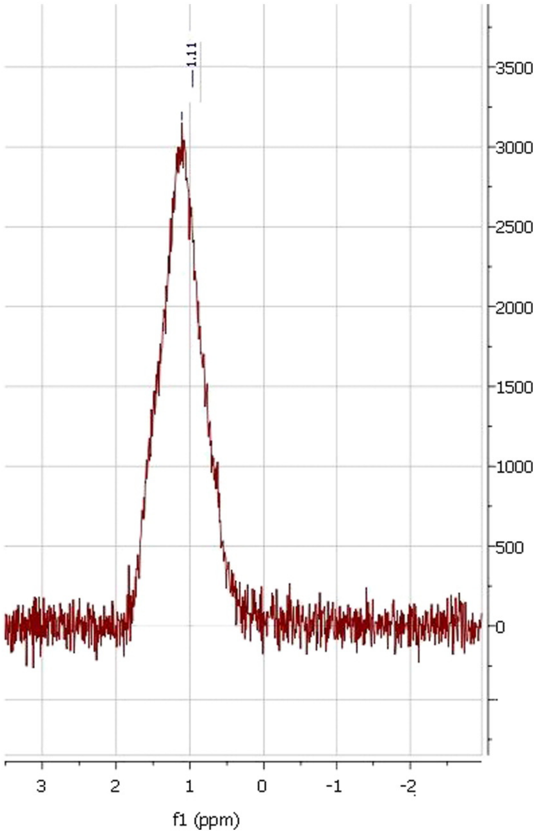


Fig. 8. ^{31}P NMR of Ph-Me(p).

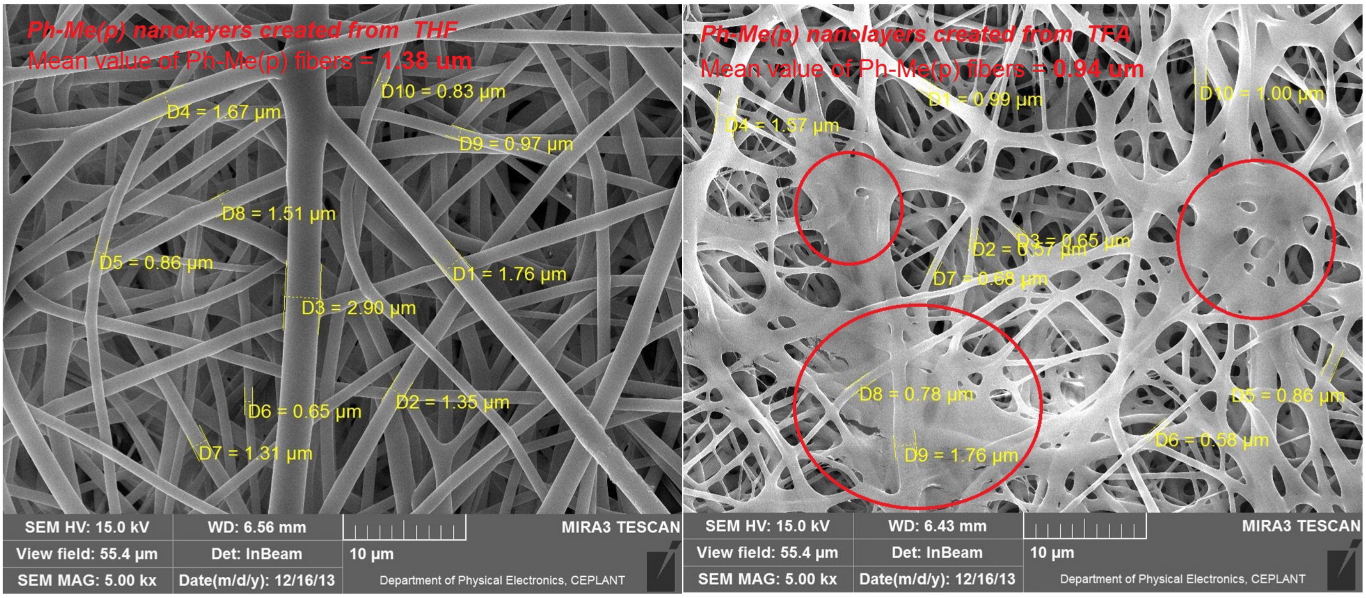


Fig. 9. SEM analysis of nanofibers from Ph-Me(p).

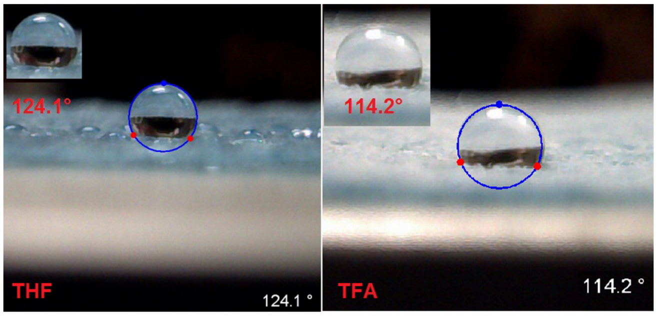


Fig. 10. *SEE system analysis of Ph-Me(p) nanolayers.*

on the fact that some polymers bear reactive groups or bonds (PA6–NH groups, SAN and ASA–CN groups and PESU has oxygen bridge in the backbone) while PS is relatively unreactive. It is probable that decomposed Ph-Me(t) in the form of short reactive linear chain, interacts with reactive groups of PA6, SAN, ASA and PESU. Then, such modified polymers are predisposed to the easier decomposing of polymers/copolymers backbone which is confirmed by lower T_d^a. The PS backbone is relatively unreactive and so the effect of possible reaction between PS backbone and decomposed Ph-Me(t) is not observed.

4. Conclusion

The phosphazene derivative Ph-Me(t) was used as an additive in commercial polymers (PA6, PS, SAN, ASA, PESU) to form more hydrophobic nanofiber materials created by electrospinning technology. The polymeric form, Ph-Me(p) especially spun from THF, is an even more suitable variety for creating layers which are more hydrophobic and more thermal stable in a comparison with Ph-Me(t). It has been discovered that the presence of the additive Ph-Me(t) can positively increase the hydrophobicity of organic polymeric fibers, although the hydrophobic character of the commercial polymer itself has a greater impact on the resulting value of the water contact angle.

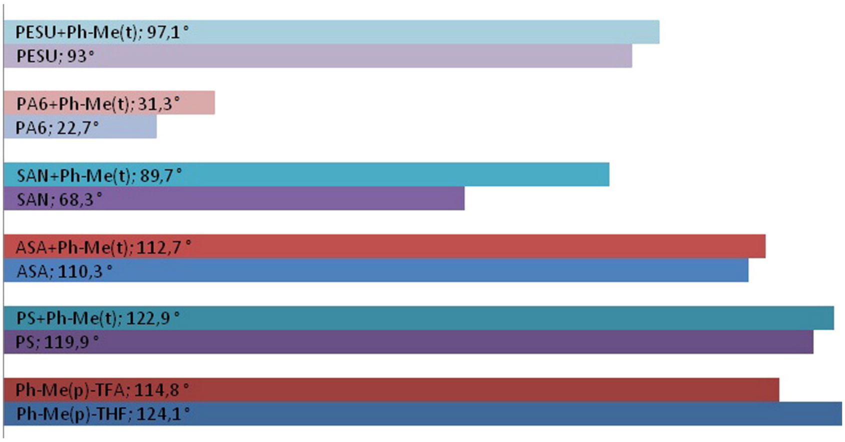


Fig. 11. The comparison of contact angles values measured on the nanolayer samples (Fibers 1, 2, 3).

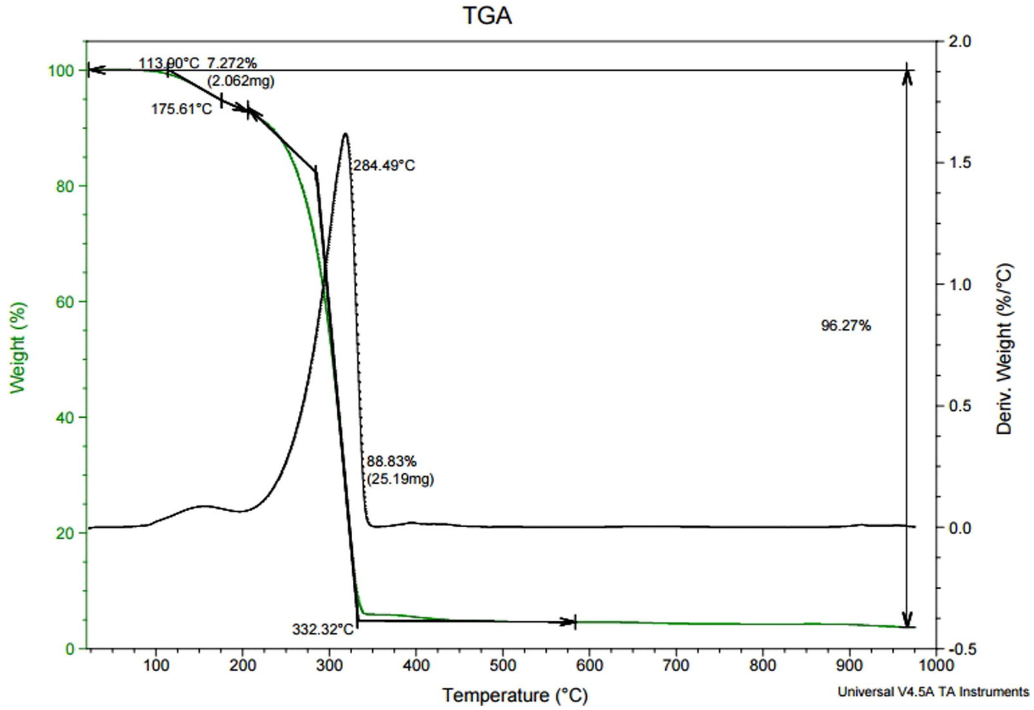


Fig. 12. TGA curves of Ph-Me(t).

Higher contact angle values were obtained for nanolayers in the presence of the Ph-Me(t) additive (in combination with all the aforementioned commercial polymers = Fibers 2) than for nanolayers made only from commercial polymers without the Ph-Me(t) additive (Fibers 1). The mere fact that nanofibers can be created from commercial polymers enriched with the Ph-Me(t) additive leads to the expansion of their application possibilities.

Although the use of Ph-Me(t) in commercial polymers improves the hydrophobic properties of nanofibers, it has been proposed to use Ph-Me(p) itself as a material for forming nanofibers. Ph-Me(p) dissolved in THF can be electrospun into homogenic nanofibers which exhibit better hydrophobic properties and higher thermal stability than the other nanofibers described above.

It must also be mentioned that the synthesis of Ph-Me(p) is more complicated than the synthesis of Ph-Me(t) and so it must be considered, whether to use the combination of organic polymers and the Ph-Me(t) additive or whether using Ph-Me(p) itself for creating nanofibers is more suitable for practical application.

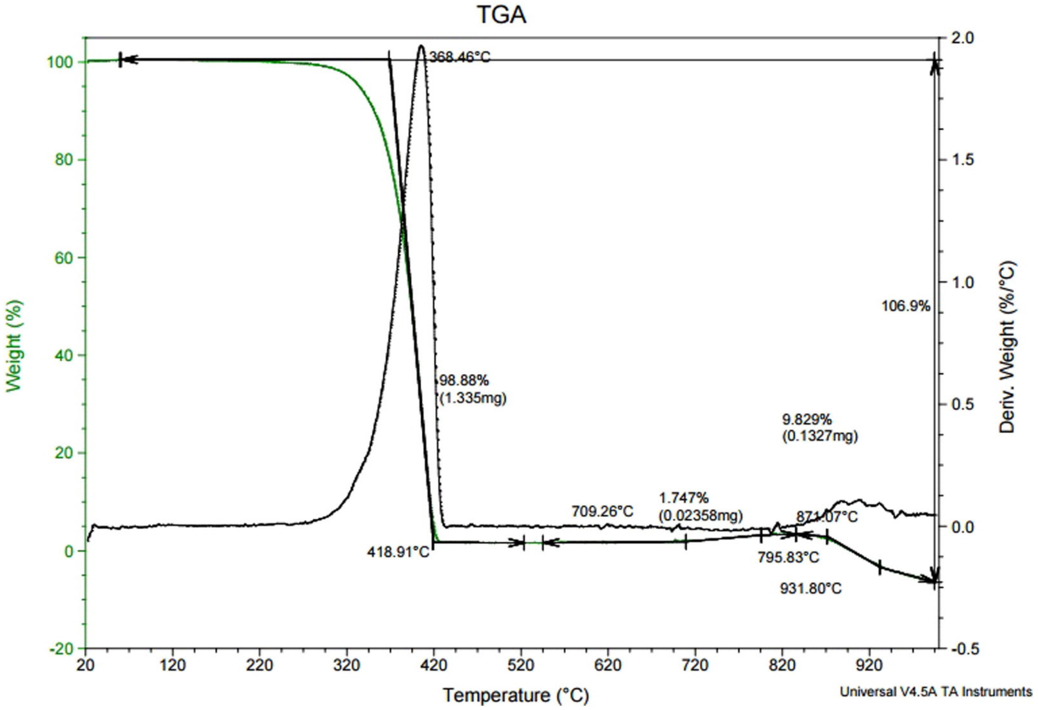


Fig. 13. TGA curves of Ph-Me(p).

Table 4
The comparison of minimum thermal decomposition temperatures from TGA for polymeric nanofibers with and without Ph-Me(t).

Fibers composition	T_d^a (°C)	$T_d{}^a{}_{\text{polymer}} - T_d{}^a{}_{\text{polymer+Ph-Me(t)}}$
PA6	342	−189 °C
PA6 + Ph-Me(t)	153	
PS	200	+10 °C
PS + Ph-Me(t)	210	
ASA	210	−120 °C
ASA + Ph-Me(t)	90	
SAN	230	−5 °C
SAN + Ph-Me(t)	225	
PESU	320	−210 °C
PESU + Ph-Me(t)	110	

T_d^a = Minimum thermal decomposition temperature from TGA.
−/+ = the value of decrease/increase of T_d^a.

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