FROM SYNTHESIS TO APPLICATION. POLYURETHANE NANOFIBERS DEVELOPED IN SPUR a.s.

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Abstract

Electrospinning is technology, which can be used for production of nanofibres and nanofibers based composites. One the main disadvantage of nanofiber based structures is their weakness. This undesirable property can be improved by the use of suitable polymers such as polyurethanes (PU) which have high elasticity. The specific attention has been paid to synthesis type, chemical composition of PU, stability of PU solution during electrospinning process, rheological analysis of electrospinning process efficiency, quality/property changes of the produced nanofibers as well as nanolayers homogeneity, application for liquid and gaseous filtration being the reason. Selected properties of PU nanofibre layers prepared during several hours of manufacture in optimized electrospinning process are proved on the results from the aerosol filtration.

The appearance of nanowebs in polyurethanes/multiwalled carbon nanotube composite nanofibers containing structures from PU nanofibers with diameters of 20-40 nm is discussed too.

1. INTRODUCTION

Weakness of nanofiber based structures prepared by electrospinning [1-15] is improved by the use of polyurethanes (PU) which have high elasticity. PUs are segmented polyadducts build-up from soft (polyol) and hard (created from diisocyanate and chain extender) segments. In the first part of this work, the process stability/efficiency with respect to final nanofiber product quality was investigated.

Filters for mask are generally based on cellulose materials. Application of PU nanofibers for filters requests several optimization steps which are discussed in the second part of the work finished with filter end product properties.

2. EXPERIMENTAL

Nanofibers were prepared from PU solutions in dimethylformamide (DMF) by using commercially available Nanospider equipment (http://www.elmarco.com) employing one rotational electrode with needles. Experimental conditions (approximation 1-4) were as follow: Relative humidity RH ~ 29 %, temperature T ~ 25°C, electric voltage U = 75 kV, distance between rotating and static electrode L = 18 cm, electrode spin R = 7 r/min., speed of antistatic polypropylene nonwoven fabric collecting nanofibres S = 0,16 m/min. PU solutions in DMF were synthesized from 4,4'-methylenediisocyanate (MDI), polymer diol (Mn ~
2.10^3) and 1,4-butanediol (BD) in molar ratio 6:1:5 (9:1:8 eventually) at 90°C for 5 hours. The following polymer diols, which introduces different type of soft segments in PU, were used: polytetramethyleneoxide (PTMO), poly(1,4-butanediol)-co-(adipic acid) (PBA), poly(3-methyl-1,5-pentanediol)-alt-(adipic, isophthalic acid) (PAIM), poly(3-methyl-1,5-pentanediol)-co-(adipic acid) (PAM) and copolymer based on diethyl ester carbonic acid with 1,6-hexanediol and 3-methyl-1,5-pentanediol (PCHM). All PU solution viscosities (η) were adjusted to be equal to 1.5 Pa.s (which corresponds to PU 10.5-15.8 wt.% concentration in DMF) having conductivity χ ~ 150 ìS/cm (adjusted by tetraethylammonium bromide). PUs were synthesized firstly in “One shot” (Os) where all reactants were added in one step and secondly “Per partes” (Pp) where the prepolymer was synthesized from MDI and polymer diol (molar ratio 2:1) firstly and in the second step, all extender (BD) was added and remaining MDI quantity was added after 1 hour of polyaddition reaction.

The PUs before and after the process were analyzed rheologically by using rotational rheometer ARES 2000 whereas nanofiber structure analyses have been done by using Scanning Electron Microscope JSM 840 (JEOL). With the aim of analyzing the presence of carbon nanotubes in PU nanofibers the transmission electron microscopy (TEM JEM 2010, JEOL) was used.

Tested mask filters were prepared by course of filters manufacture in Sigma Lutín (including folding of nanolayer based filtrating materials). Penetration of aerosol at flow 30 l/min. (5.7 cm/s) was measured by means of filter measuring system LORENZ adjusted for EN 143.

3. RESULTS AND DISCUSSION

Structural stability/changes of the PU solution during the electrospinning process and product manufacture quality are discussed here in more details. PU samples before the process, after several hours of the process and PU samples which nanofibres are created from where analyzed rheologically and relaxation spectra were determined for all of them from frequency dependent loss and storage moduli measurements. The results are depicted in Figures 1-8.

Quality control of manufactured nanolayers, optimization steps for application of nanolayers in filters (including the influence of selected variables), properties of mask filters prepared by means of nanolayers and discussion about possible exploitation of nanowebs are presented in Figures 9 – 23 and approximations 4 – 8.

1. approximation – synthesis optimalization, stationary electrospinning process

Set of PU samples, containing PBA soft segment, with varying molar ratio MDI:PBA:BD from 2:1:1 to 6:1:5, were synthesized and fibrillated in electric field. The best nanofibres quality was reached from molar ratio 6:1:5 and that is why the PU based on other polymer diols were synthesized with the same molar ratio.

In Figure 1 it can be seen that relaxation spectrum for PTMO based PUs (prepared by Os synthesis) differ significantly if the PU samples taken before and after 3 hours of the process are compared. In this case, the quality of the produced nanofibers was change in the time as well. On the other hand, PTMO based PU (prepared by Pp synthesis) has shown no big differences in the quality of the produced nanofibers during 3 hours process which is reflected by no big changes in the relaxation spectra for original and processed PU samples (see Figure 2).
2. approximation – influence of soft segments chemical composition

In Figures 3-5, the relaxation spectra for original and processed PU samples prepared by Pp syntheses, having different types of the soft segments, are depicted. It has been revealed that PUs with PAIM and PCHM soft segments were the best from the time dependent stability and nanofibers quality point of view. It has been found that it correlates very well with low variation in the relaxation spectra within the processing time as visible in Figures 4-5.

3. approximation – rheological properties comparison of PU in treated solution and nanofibres

Relaxation spectra comparison of PUs from spinning bath and fibrillated PU (samples were prepared by dissolving of nanofibres and subsequent evaporation of DMF) prove the best workability for PU with PAIM soft segment. Such a PU can be used in long term electrospinning process and even for close-cycle
technology. Spectra of PUs from nanofibres show constant values of elastic modulus in wide interval of relaxation times, the formation of double linkage conjugated system in PU chains (connected also with browning of PU) being the reason.

Figure 6 illustrates the changes in quality of nanofibers which were detected by rheology analysis. Process efficiency (expressed as dependence of area mass on concentration of PU in solution) decrease with process duration in case of bigger variation in relaxation spectra.

Figure 9 illustrates the changes in quality of nanofibers which were detected by rheology analysis. Process efficiency (expressed as dependence of area mass on concentration of PU in solution) decrease with process duration in case of bigger variation in relaxation spectra.

Fig. 6. Relaxation spectra of PUs based on PAM, comparison of PUs from fibrillated solution and nanofibres.

Fig. 7. Relaxation spectra of PUs based on PCHM, comparison of PUs from fibrillated solution and nanofibres.

Fig. 8. Relaxation spectra of PUs based on PAIM, comparison of PUs from fibrillated solution and nanofibres.

Fig. 9. Changes of area mass with process duration, influence of soft segments chemical composition.
4. approximation – product manufacture quality and properties changes during spinning process

One of the easiest but very large application of layers based on nanofibres is filtration. Uniformity of nanofibres deposition during several hours of process was traced by means of SEM (Figures 10–12), by measurement of area mass, nanofibres distribution (Figures 13-14) and capture of aerosol particles under EN 143 characterized by pressure resistance and aerosol penetration [15]. We have found minimum differences in filtration properties during 3 hours electrospinning process.

**Fig. 11.** Nanofibres made of PU 615 based on PAIM after 175 min. of electrospinning process.

**Fig. 13.** Nanofibres distribution after 85 min. of process. Area mass = 1.278 g/m$^2$, thickness = 3.6 µm, average fiber diameter = 198 nm, pressure drop = 316 Pa, aerosol penetration ~ 0.01%.

5. approximation – influence of fiber diameter
A lot of useful information can be obtained by theoretical modeling of filtrating process [16-17]. One of the variables which directly influence the filtrating efficiency of nanolayer is nanofiber diameter. General influences of PU solution conductivity, concentration, used voltage and distance between rotating and static electrode on nanofiber diameter at electrospinning are depicted on Figures 15 – 18.

![Influence of voltage](image1)

**Fig. 15.** Dependence of fiber diameters on voltage changes. Aluminum foil and PP nonwoven collecting support.

![Influence of electrode distance](image2)

**Fig. 16.** Dependence of fiber diameters on distance between rotating and collecting electrode. Aluminum foil and PP nonwoven collecting support.

![Influence of polymer concentration](image3)

**Fig. 17.** Dependence of fiber diameters on concentration of PU solution.

![Influence of solution conductivity](image4)

**Fig. 18.** Dependence of fiber diameters on conductivity of PU solution.

6. approximation – sense of optimization

Electrospinning is very sensitive process with plenty of variables which have to be combined in direct way. We concentrated on the preparation of homogeneous, thin but sufficiently tough nanolayers exhibiting the same properties during the whole electrospinning process, to reach material with minimum pressure drop and minimum aerosol penetration. Requested properties changes reached by optimization of nanolayers
preparation are plotted on Figures 19 and 20 and summarized in Table 1. By using origin PU it would be necessary to apply nanolayers with 5 times higher area mass then in case of optimized PU to reach the same aerosol penetration (Figure 19, \( \ln(\text{aerosol penetration } 0.0009\%) = -7 \)).

![Aerosol penetration vs Area mass](image1)

![Pressure drop vs Area mass](image2)

Fig. 19. Changes in aerosol penetration after optimization of PU solution properties and processing conditions.

Fig. 20. Changes in pressure drop after optimization of PU solution properties and processing conditions.

7. approximation – manufacture of filters

All filters containing nanolayers prepared by optimized way of manufactured exhibit good aerosol penetration (much better then requested by EN 143 class P3). It seems that application of nanofibers will make possible the preparation of filters with lower pressure drop thus one of two more important filtrating characteristics (Table 1).

Table 1. Optimization of filter manufacture

<table>
<thead>
<tr>
<th>Optimization step</th>
<th>Area mass of nanolayer (g/m²)</th>
<th>Pressure drop (Pa)</th>
<th>Aerosol penetration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Request on filter P3 according to EN 143</td>
<td>-</td>
<td>120</td>
<td>0.05</td>
</tr>
<tr>
<td>Before optimization process</td>
<td>4.25</td>
<td>46</td>
<td>0.7362</td>
</tr>
<tr>
<td>After nanofiber average optimization</td>
<td>2.81</td>
<td>87</td>
<td>0.0061</td>
</tr>
<tr>
<td>After nanolayers homogenization</td>
<td>1.35</td>
<td>63</td>
<td>0.0097</td>
</tr>
<tr>
<td>After nanolayers lay down optimization</td>
<td>1.52</td>
<td>46</td>
<td>0.0069</td>
</tr>
</tbody>
</table>
8. approximation – formation of nanowebs

Filtrating efficiency of nanolayers could be improved by formation of nanowebs (spider-net within nanofibers) in nanofibrous morphology. Creation of such a nanostructure we have discovered for the first time at preparation of PU based nanofiber composites with multi wall carbon nanotubes [14]. Nanowebs improve also the mechanical properties [18] which is highly desirable for stress application.

CONCLUSIONS

The first technological request for potential application of layers from nanofibres is production of material with constant properties during the whole continues manufacture. It has been revealed experimentally that an application of PU based on PAIM soft segment satisfies this important technological request. It has also been found that rheological analysis of PU, treated in electrospinning process, can be useful tool from process efficiency and optimization point of view.

Filters prepared by means of PU nanolayers easily reach the properties requested by EN 143 and open the space for manufacture of filters with balanced filtrating properties.

REFERENCES

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