LOW-COST MANUFACTURING OF BATTERY SEPARATORS ON THE BASE OF POLYPROPYLENE NONWOVEN FABRICS

Ľ. Černáková¹, J. Ráhel², D. Kováčik², <u>M. Černák³</u>

¹ Slovak University of Technology – Department of Plastics and Rubber, 812 37 Bratislava ² Comenius University – Department of Experimental Physics, 842 48 Bratislava ³ Masaryk University – Department of Physical Electronics, 611 37 Brno

Introduction

Rechargeable alkaline batteries typically require separators to function primarily as dielectric as well as electrolyte reservoirs. In addition to being inert to 31% potassium hydroxide (KOH) used as the electrolyte, separator materials should posses durable wettability to withstand the rigors during the discharging and recharging the battery. Typical separator constructions employ nonwoven structures comprising either polyamide or polyolefin fibers: Polyamide resin fibers are excellent in mechanical strength, gas permeability, and electrolyte absorption but poor in alkali resistance and oxidation resistance. Accordingly, under severe battery use conditions such as high temperature or extremely long use, those materials are decreased in mechanical strength as a separator, which leads to the induction of short-circuiting inside the battery including such separator material. Furthermore, if this battery is stored in a high temperature environment or is exposed to frequent overcharges that would cause evolution of oxygen gas, the polyamide resin fibers constituting the separator may be decomposed.

Therefore, surface modified polyolefin, and in particular polypropylene (PP), nonwovens have been drawing attention as a material for separators that has adequate heat-resistance and does not decompose even in a high concentration of alkaline electrolyte at high temperature [1,2]. The surface modification ("hydrophylization") is necessary to make the inherently hydrophobic poleolefin fibers hydrophilic so that the aqueous electrolyte will wet out the separator. Known surface modification techniques are, for example, surface treatment of resin fibers with a surfactant, sulfonation and fluorination. Of particular concern and commercial success is the surface modification of using UV graft copolymerization by acrylic acid (AA) developed by SciMAT Limited [2,3]. Nevertheless, although successful commercially, this process has the disadvantages of using surfactant and organic solvensts to ensure that the grafting solution fully impregnates the PP nonwoven fabric.

An environmentally and economicaly attractive alternative to the above mentioned processes is the low-temperature atmospheric-pressure plasma surface activation of PP nonwovens, where polar molecular fragments affecting the wettability and radicals serving as the reactive species for the graft polymerization are formed on the fabric fiber surfaces. The plasma surface activation makes possible to use water-based catalyst-free grafting solutions having good operability and properties to environment.

In the present contribution we will report preliminary results obtained using a proprietary atmospheric-pressure plasmachemical reactor (see Fig. 1) designed for atmospheric-pressure plasma treatment of fabrics [4, 5]. The reactor has the unique capability for online plasma activation and polymerisation of fabrics without the use of expensive helium containing plasma gas and the treatment cost efficiency, as well as the device lifetime and robustness achieved by this technique is unmatched by any other plasma processing technology.

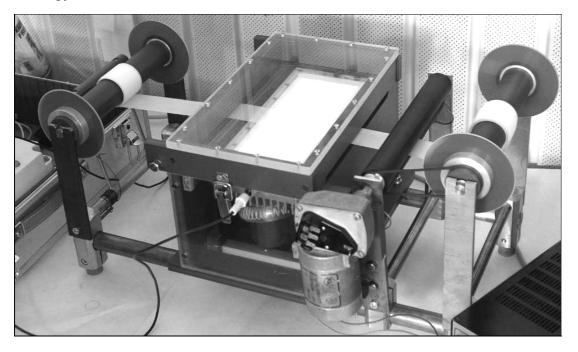


Fig. 1 Bench-scale plasma reactor for on-line surface activation of fabrics

Experimental

The plasma activation of PP spunbonded nonwovens of 50 g/m² square weights with a thickness of 280 μ m, average pore size 38 μ m, and porosity of 78% was performed by 5 seconds exposure to atmospheric-pressure nitrogen plasma gas. Surface radicals generated by the plasma activation were utilized as reactive species for subsequent acrylic acid (AAc) grafting in aqueous solution. The grafting method used was identical to that described by Seto et al. [6]: The samples were immersed into a 10 wt.-% aqueous solution of AAc in a glass ampoule. After deareating by nitrogen bubbling through, the ampoule was sealed and the grafting was carried out for 1 h at a temperature of 60°C. PAAc homopolymers were removed by washing in distilled hot water and air-dried. The surface properties of the AAc grafted PP nonwovens were characterized by scanning electron microscopy. (ESM)

electron microscopy (ESM), Fourier transform infrared spectroscopy, electron spin resonance spectroscopy, and dyeability measurements. Standard industrial test methods have been used in determining the 31% KOH electrolyte transport capabilities of the samples: The strike – through time of 3 sec and electrolyte absorption of 400 % were measured. The 60 sec and 600 sec wicking rates were 45 mm and 110 mm, respectively.

Results and Conclusion

SEM photographs of the fibers of untreated and post-nitrogen-plasma-grafted PP nonwovens are shown in Fig. 2. The energy consumption for the nitrogen plasma activation was as low as 0.9 kWh per 1 kg of 50 gsm PP nonwoven fabrics. Note that SEM examination did not reveal any changes on the fiber suface due to the nitrogen plasma activation.

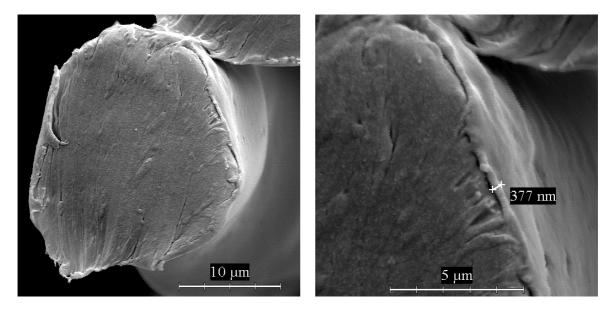


Fig. 2 Cross-section of a fibre of 50 gsm PP nonwoven fabrics grafted by 377 nm thick pAA layer.

It is believed that the results obtained indicate significant commercial potential of the method and device for on-line plasma activation and post-plasma grafting of pAA onto surfaces of PP nonwovens for the battery separator applications.

References

- 1. W. M. Choi: "Battery performance of surface modified separator" *Battery Conference on Applications and Advances* (2002). The Seventeenth Annual, Long Beach, CA, USA, pp. 83-88.
- 2. J. Cook and I. Smith: "Surface Modification of Polymeric Films and Fabrics by UV Graft Copolymerization" *Coating* (2003) pp.1-5.
- 3. J. Cook et al.: "Non-woven fabrics treatment" *Patent WO9858111* (Scimat Ltd., November 1998).
- 4. M. Černák: "Method and apparatus for treatment of textile materials" *Int. Patent Appl.* No.PCT/SK02/000008 (WO 02/095115, USP Appl. 20040194223).
- 5. M. Šimor, J. Ráheľ, P. Vojtek, M. Černák, A. Brablec: "Atmospheric-pressure diffuse coplanar surface discharge for surface treatments" *Appl. Phys. Lett.* **81** (2002) pp.2716.
- 6. F. Seto, Y. Muraoka, N. Sakamoto, A. Kishida, M. Akashi: "Surface modification of synthetic fiber nonwoven fabrics with poly(acrylic acid) chains prepared by corona discharge induced grafting" *Die Angewandte Makromolekulare Chemie* **266** (1999) pp.56-62.