Abstract - In this work, the charge storage of polyphenylene ether (PPE) based blends has been evaluated and related to the blend morphology as well as to the charging method. Binary PPE/polystyrene (PS) blends and ternary blends containing PPE, PS and poly(styrene-isobutylene-styrene) (SIBS) or poly(styrene-ethylene-1,2-butylene-styrene) (SEBS) were prepared. The PPE/PS materials showed an outstanding charge storage behavior after annealing at 90 °C. The performance of the ternary blends was function of the blend composition, the final morphology and the chemical structure of the components. Additionally, the materials were processed into thin fibrous webs using the electrospinning technique. Through electrospinning, charged fibers with diameters as thin as few nanometers can be obtained. The residual surface potential of the electrospun fibers was evaluated and related to the fiber structure as well as to the blend properties. It was found that the non-wovens were able to retain large amounts of the initial surface potential after several weeks of annealing at 120 °C and that the charge retention is highly determined by the proximity of the glass transition temperature of the polymers.

Keywords: charge storage, polymer blends, electrospinning

Introduction

Polymer electrets are of key importance for a significant number of modern devices, including transducers, microphones, air filters as well as biomedical components such as heart valves and bone implants [1]. Electret filters use electrostatic attraction as filtration mechanism and their high efficiency is primarily attributed to the fact that the charged fibers can attract both particles of opposite and neutral charge, when a dipole is induced by the charges on the fibers [2]. For all these applications, both the thermal as well as the mechanical stability are demanding factors which determine the selection of appropriate electret materials.

Previous investigations in our laboratory have demonstrated that amorphous PPE, also known as poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), has excellent charge storage performance at 90 °C. Besides of that, PPE has the advantages of having a high dielectric strength, excellent mechanical and thermal properties and, most importantly, a low moisture absorption. Nevertheless, the melt processing of PPE is limited by its high susceptibility to suffer oxidative degradation [3]. Blending PPE with polystyrene (PS) is an efficient approach to improve its melt processability, to limit the oxidative degradation, because of the possibility to process the PPE/PS blend at lower temperatures,
and to reduce its price [3]. PPE/PS blends are generally considered to be miscible across the whole composition range [4].

Polymer blends can potentially show a higher charge storage capability than the neat constituents, since the phase boundaries between the individual components can act as trapping sites [5]. In this work, the charge storage behavior of PPE is enhanced by the addition of selected amounts of PS and SIBS or SEBS. While the binary blends PPE/PS are miscible and are expected to form one homogeneous phase, the ternary blends are multiphasic. The influence of the polymer morphology on the charge storage properties will be studied. Additionally, the charge storage performance of compact films will be compared with that of non-wovens, produced and charged using electrospinning. Non-wovens based on PPE have the potential of being used as electret filters under extreme conditions such as high or low temperatures or aggressive media.

**Experimental**

*Blend preparation*

Blends of PPE and PS with PPE weight fractions of 75, 50, and 25 % were prepared by melt-compounding using a co-rotating twin-screw extruder (Brabender DSE 20/40), followed by hot-pressing at 240 °C. The ternary blends were prepared by melt-compounding PPE with 25 wt.% of PS and amounts of SIBS or SEBS varying between 2.5 and 20 wt.%. Afterwards, films of 100 µm were prepared by hot pressing at 240 °C.

*Surface potential measurements*

Comparative Isothermal Potential Decay measurements were performed on films of 4 × 4 cm², attached to aluminium substrates using a conductive carbon adhesive tape of thickness 0.16 mm and a resistivity < 5 Ωm. Firstly, the films were positively or negatively charged for 10 s using a custom-build point-to-plate corona setup (tip-to-mesh distance = 8 cm; mesh-to-specimen distance = 5 mm) in order to ensure a homogeneous electric field across the film surface area. A corona voltage of +12.5 kV and a mesh voltage of +0.4 kV were applied, leading to uniform surface potentials between ± 380 and ± 420 V. The surface potentials (V) were measured using an electrostatic voltmeter (Monroe Electrostatic Voltmeter 244A) with a sensor-to-specimen gap of about 2 mm. The first measurement (V₀) was taken directly after charging at room temperature; all further measurements were carried out after fixed annealing times at different elevated temperatures (90, 120, and 150 °C). The average value of five measurements at different positions across the film surface was used for evaluation.
Non-woven preparation

Solutions of PPE, PS and their blends were prepared in a CHCl₃:HFIP mixture (80:20, v/v) at weight concentrations between 15 (w/v). The polymers were dissolved at room temperature after 1 – 2 h of stirring. A conventional vertical electrospinning setup was employed (see Fig. 1). A polymer solution was placed in a 5 ml syringe attached to a hydraulic pumping system that maintains a constant output of the syringe at 0.05 ml/min. In separate experiments, voltages of +40 kV and -40 kV were applied to a metal needle (inner diameter, 0.6 mm) at the end of the syringe. The counter electrode, consisting of a grounded aluminum sheet, was placed 30 cm below the needle-tip. The experiments carried out under environmental conditions (T = 25 °C and 50% relative humidity). Fixing the electrospinning time controlled the thickness of the fiber mats.

![Schematic representation of the electrospinning process](image)

Measuring the surface potential

The residual charge of the fiber mats after electrospinning was evaluated on a similar way that the compact films. A surface area of 20 x 20 mm² was scanned, and the average of the surface potential measured at nine different positions was reported. The first value of the surface potential (V₀) was taken at room temperature one hour after the mats were electrospun. Afterwards, the mats were kept at elevated temperatures (90, 120 or 140 °C) and additional measurements of the surface potential were carried out after fixed (30, 90, 180, 360 and 1440 min (24 h)) annealing times.

Results and Discussion

In Figure 2, the surface potential decay of positively charged PPE/PS blends as function of the annealing time at 90 °C is presented. Interestingly, the two blends with PPE contents of 50 wt.% and higher only loose less than 10 % of the initial surface potential after 24 h of annealing, as such revealing a superior performance at 90 °C as compared to the neat PPE. Additionally, the addition of 25 wt.% of PS to PPE, increased the amount of charge retained from 60 % to 77 % after 24 h at
120 °C. This experimental observation indicates a synergistic behavior unexpected from a rule-of-mixture approach.

Such result was associated with two particular morphological characteristics. Firstly, the blends showed a heightened density packaging on a molecular level that limited molecular mobility and effectively reduced the charge drift. Secondly, micro-heterogeneities and local fluctuations in blend composition were detected in the mixed phase; the resulting nano-scale phase boundaries might also acted as charge traps and, thus, restricted the charge decay of the blends as compared to the neat materials. These findings highlight that the electret performance is affected by molecular mobility and molecular heterogeneity.

Since blending increases the heterogeneity of the polymer morphology, it is of interest to study the charge storage retention of ternary blends based on PPE. The blend composition, the final morphology and the chemical structure of the components have an influence on the electret performance. As presented in Figure 3, when copolymers of relatively low molecular weight are added to the PPE/PS blend, they coalesce rapidly during processing, forming networks that are used by the charges as pathways for a quick discharge of the material. It was obtained that the charge storage capability is favored by a finely dispersed and non-interconnected phase, but can be reduced by the high polarity or low molecular weight of the blend components.
Electrospinning allows the preparation of charged fibers with diameters in the nanometer order. The time stability of the charge on the fiber surface is an indication of the electret properties of the polymer. As shown in Figure 4, the fiber mats presented a much more stable surface potential in comparison to the corona-charged compact films. Compact films of the 75/25 PPE/PS blend were able to retain 74% of the initial charge after 24 h at 120 °C but showed a rapid decay (to only 10%) when the annealing temperature was increased to 140°C. In contrast, the fiber mats of this material retained up to 60% of the initial charge after 72 h at the same temperature.

In the electrospinning process, the charge is injected into the solution before the fiber is even formed, so it can be expected that the charges are located in the deep trapping levels of the bulk state which might explain their higher stability. Furthermore, the corona charging process of the films was performed at room temperature, which mainly leads to the trapping of real charges, as the orientation of the dipoles is limited by the solid state of the material. In contrast, in electrospinning, in addition to the formation of real charges, it is possible to align the dipoles, as the material is solvated during the charging process. These dipoles will remain aligned as the material solidifies and are recognized as one of the main polarization mechanisms in polymers with polar groups like PPE.
In summary, in the electrospun fiber mats, two charge storage mechanisms are combined: real charges located in deep traps in the bulk of the material and permanently oriented dipoles in the PPE phase.

**Conclusion**

The generally poor melt processability of PPE can be overcome by blending with polystyrene; an approach that simultaneously leads to further enhanced electret properties of blends containing a high PPE weight fraction. But the potential of blending to enhance charge storage properties was further exploited by the preparation of ternary blends. Within this approach, a finely dispersed and non-interconnected phase favored the charge storage capability. Indeed, the ternary 75/25/2.5 PPE/PS/SIBS blend showed 37% more retained charge than neat PPE after 24 h at 120 °C. By using electrospinning, it was possible to prepare and electrostatically charge the fibers in one single step. The charge retention of the PPE/PS spun fiber mats is notably higher than that of the corona-charged compact films, which reveals the capacity of electrospinning to inject charges into the bulk of the material, and to orientate the dipoles of the PPE phase in the field direction at the same time. PPE/PS blends with 25 and 50 wt.% PS show a good combination of electrospinnability, fine fibers and charge retention properties, displaying their potential for electret filter and sensing applications.

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