PP-based blends for electret filters - an appraisal

J. VAN TURNHOUT*, P.J. DROPPERT*, and M. WÜBBENHORST**

* TNO - Plastics and Rubber Research Institute, P.O. Box 6031, 2600 JA Delft, The Netherlands

**Dept. of Polymer Technology, Delft University of Technology, P.O. Box 5045, 2600 GA Delft, The Netherlands.

Abstract

Corona-charged polypropylene-based polymeric materials for electret filters were studied. Blending of PP with polycarbonate was found not to improve its performance, despite claims made elsewhere.

The electret properties were characterized with several techniques, including one that allows the determination of the fine structure of all trap-depth energies.

Trapping near the crystallites provides most of the deep traps in PP-based polymers. A more perfect crystallite structure thus enhances the charge stability. This fact offers better opportunities for producing longlasting electret filters than blending with PC.

A crucial factor is that the PP-blend should remain nonpolar in order to guarantee a low conductivity and high water repellency.

1. Introduction

The successful application of electret fibres in air filters heavily relies on a proper choice of the polymeric material. In this paper we will focus on polymeric materials for electret split fibres. For several years electret split fibre filters (Filtrete®) have been produced by 3M using PP as the base material. Recently, Mitsui has launched electret split fibre filters (Syntex EL®) based on a blend of PP and PC (Blendmer), which they claim perform better [1].

This prompted us to make a thorough study of the filtration characteristics and the electret properties of such a blend. We hereby used regular PP as a reference.

Since PP and PC are not miscible, the blend also contains a compatibilizer PP-g-MAH (i.e. PP onto which a few maleinic anhydride groups have been grafted). Chemical analysis has shown that the blend consists of 90 wt% PP, 5 wt% PC and 5 wt% PP-g-MAH. Admittedly, for charge storage rather the molar ratios count; they are 99.09 mol% PP, 0.85 mol% PC and 0.06 mol% MAH. The number of MAH-groups in the mixing promotor PP-g-MAH is only 1 MAH to 77 propylene units, since the molar fraction is 1.3 mol%.

Apart from good electret properties, the polymeric material for electret split fibres should also have special mechanical properties. The reason being that fibrillation into fine fibres forms an essential part of the production process; this is achieved after stretching the extruded film by over 6x. A polymer like isotactic PP can then be nicely split or fibrillated, e.g. with a needle roller; see [2] for further details.

It is well established that electrets of which the external field is used, such as in filters or microphones, should be produced from a **nonpolar** material [3]. The major benefits are that the electrets can then be made by corona charging (so at a high speed) and that the electrets show a long lifetime even under harse conditions of high humidity and high temperature. Electrets made from polar polymers are known to perform notoriously bad under such conditions.

2. Why a blend with PC ?

This choice may well have been spurred by the patent situation. In [4] it was claimed that the polymeric material should be nonpolar. We will return to the question whether the addition of 0.85 mol% PC and 0.06 mol% MAH really converts PP into a polar material later.

As stated in their patents [1] Mitsui claims that the dispersed PC particles would provide extra trapping sites. However, PP being semi-crystalline is already a heterogeneous material; it contains plenty of small crystallites, which are known to form very effective sites for persistent charge storage [3]. The numbers of traps available in unblended PP is therefore more than sufficient.

Mitsui's rationale is further that the few carbonate dipoles supplied by the PC would create a heterocharge and would in this way improve the charge stability. One can readily show that this will not be the case either. Any dipole present will in fact destabilize a corona charged electret. Because during the very short corona charging at room temperature, only some of the dipoles will get oriented; the remaining will try to do so later on, forced by the internal field created by the strong real (homo)charge deposited by the corona. The dipoles will thus gradually build up an opposite (hetero)charge and so speed up the decay of the total charge rather than slow it down, see Fig.1.

Fig.1 Calculated isothermal decay of a corona charged electret with and without some dipoles present. Since the dipoles are too slow to orient during the brief charging, they will do so afterwards. They will thus lower the total charge rather than increase it.

In practice, this destabilization remains small, because the carbonate dipoles in PC are virtually immobile, unless the temperature draws closer to the glass-rubber transition of PC (150°). On the other hand, the MAH-dipoles being attached to the flexible PP-chain are quite mobile at room temperature; their concentration is however too low to do serious harm.

Quite another role suggested for the few MAH-groups present is that they would act as a local charge trapping site. However, this too is very unlikely, for the following reasons, see also Fig.2:

- 1° being a polar group, MAH can never exert a strong binding force on an electron or a hole,
- 2° being an acid residue, hole trapping is even all the more unlikely^{*1}

^{*1}Stable positive charge trapping is however essential in the bipolarly charged electret fibres.

3° being linked to the flexible PP-chain, MAH rotates almost freely in the blend at 25°C (T_g of PP is -2°C !). This excludes any stable trapping.

Fig.2 a) Structure of the PP-g-MAH compatibilizer. b) Illustration that a polar group, with its positive and negative end close together, can never form a strong binding, deep trap; in particular not if it rotates vividly.

On these grounds one cannot expect that blending of PP with PC will lead to a better product. Let us now consider the experimental facts.

3. Experimental results

In this section only the electret/electrical properties will be discussed, although it should be mentioned that the filtration characteristics of the PP-PC blend turned out to be somewhat inferior to those of PP.

The thermal charge stability of electret materials is of course an important quantity. This can be ascertained best with charge TSD, in which the charge retention is measured as a function of temperature during a linear scan [5]. The results are shown in Fig.3. Clearly, no superiority of the PP-PC blend can be seen.

Fig.3 Charge TSD of extruded films of PP and of the PP-PC blend corona charged at 25°C. The heating rate was 1°C/min.

Apparently, the charge storage and charge stability in the PP-PC blend are still dictated by its PP-matrix with its favourable electret properties. This is not surprising, since PP accounts for 99.1 mol%.

The good charge retention of nonpolar polymers like PP derives from 2 properties:

- 1° a very low conduction, so that the dissipation of charges by free ionic species is low,
- 2° presence of deep trapping sites.

Since the amorphous part of PP is in its rubbery state at 25°C, the trapping is centred near the crystallites. They form up to the melting point very effective road blocks that impede the charge transport and thus charge neutralization enormously. Hence, the more perfect the crystalline structure and the better the crystallites are aligned laterally, the better the charge

stability. It is therefore fortunate that stretching forms part of the production process.

Obviously, not only PP, but also the PP-PC blend will gain from the stretching; this is illustrated in Fig.4. These results demonstrate that the idea that the charge trapping in the blend would rely on the presence of the MAH of the compatibilizer is incorrect.

Fig.4 Beneficial effect of 5x stretching on the charge TSD of the PP-PC blend.

We mentioned already that the MAH-group is in fact too mobile to form a stable trap. This motional freedom was confirmed by current TSD and by dielectric measurements. The results are shown in Figs.5 and 6, in which MAH is seen to enhance the weak TSD current and the weak dielectric losses at the glass-rubber transition of PP.

Fig.5 Current TSP (P=polarization) and current TSD (D=depolarization) of PP-PC blend. Note that during the poling the TSP current goes negative, i.e. reverses, due to the volume expansion. ($V_p = 400V$, $A = 10.2 \text{ cm}^2$, $h = 2^\circ\text{C/min}$)

Fig.6a Dielectric permittivity of PP-PC blend at various frequencies. The curves coincide for all frequencies, because ϵ' remains constant.

Fig.6b Dielectric losses at 1kHz of PP-PC-blend (top) and PP (bottom curve). We see that the losses are extremely low, which implies that the blend is nonpolar.

This clearly reveals that the MAH-groups rotate already unhindered at the T_g of PP.

The results of Fig.6 also allow us to address the question whether the PP-PC blend should be ranked as a nonpolar material. The very fact that its dielectric constant remains constant both as a function of temperature and of frequency proves that

$$\epsilon' = n^2 \quad (1)$$

with n the refractive index. This Maxwell relation implies, according to Debye, that the material is free from dipolar losses and thus is nonpolar. The very weak dielectric losses ϵ'' of the blend are virtually the same as those of PP [6].

4. Conclusions

Our investigations have shown that blending of PP with PC does not improve the electret and filter performance of PP. A good quality PP-grade can do the job equally well or better. The claim that the addition of 0.85 mol% PC together with 0.06 mol% MAH (of the compatibilizer) would turn PP into a polar material is refuted by the experimental facts, as is the notion that MAH would provide a deep trap.

Results presented in the appendix will show that Mother Nature provides for more than enough deep traps in PP, there is no need for more.

References

- [1] Japan. Patent Appl. JP 60-225416: "High performance electret and air filter"; Europ. Patent Appl. EP 0-447 166 A2: "Process for producing an electret, a film electret, and an electret filter"
- [2] J. van Turnhout, W.J. Hoeneveld, J.W.C. Adamse, L. van Rossen: IEEE Trans. Ind. Appl. IA-17, 240-248 (1981)

- [3] G.M. Sessler ed.: "Electrets", 2nd ed. (Springer, Berlin, 1986)
- [4] US Patent 3998916/ Re 30783: "Method for the manufacture of an electret fibrous filter"
- [5] J. van Turnhout, Ch.3 in [3]
- [6] N.G. McGrum, B.E. Read, G. Williams: "Anelastic and dielectric effects in polymeric solids (Wiley, New York 1967), p.385-387
- [7] J. van Turnhout, K.E.D. Wapenaar: Ext. Abstracts 15th Europhys. Conf. on "Macromol. Physics", Hamburg (E.P.S., Geneva 1983) p.128-130

Appendix: Method to determine the fine structure of all trap-level energies.

In this method we take 2 or 3 identical film samples. Next we charge them under the same conditions to the same level and then measure their charge TSD at different heating rates h . We can then calculate two derivatives of the surface voltage V : $\partial V/\partial T$ and $\partial V/\partial \ln h$ [7].

It can be shown, e.g. on the basis of the decay equations given in [5, p.171-175], that

$$\frac{\partial V/\partial T}{\partial V/\partial \ln h} \approx \frac{A(T)}{kT^2} \quad (2)$$

where $A(T)$ is the trap-depth energy of those traps that empty at the temperature T .

The results for PP are shown in Fig.7. We notice that quite deep ("natural") traps, as deep as 2.85 eV, are present in PP. Beyond 105°C the energy decreases, because then the decay by ohmic conduction becomes more prominent.

Fig.7 Three charge TSD curves of corona-charged PP measured at different heating rates. The derivatives $\partial V/\partial T$ and $\partial V/\partial \ln h$ are also plotted, as is the trap-depth profile A vs. T calculated from their ratio.