Charge Storage Performance of Polyetherimide Ultem®1000—Influence of Secondary Antioxidants and Purification

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ABSTRACT: The performance of a polymeric electret material depends on many parameters, and besides chemical structure, charging conditions, and application temperature, other factors, such as grade, manufacturer, processing history, and additive package, are critical. Commercial polyetherimide (PEI) Ultem®1000 films exhibited satisfying electret properties as revealed by an isothermal potential decay (ITPD) to 75% of the initial surface charge after 24 h at 90°C. It was found that after purification by reprecipitation this value drops to 34% and that the same PEI synthesized by two different methods revealed to be a very poor electret with charge retention of almost zero. Assuming that an additive in the commercial material might be responsible for this behavior, we identified an organophosphonite which is commonly used as antioxidant in high-temperature polymers. We incorporated this additive by melt compounding into purified PEI and found a dramatic increase in charge retention to 79% of the initial charge at an additive load level of 0.5 wt %. By immersing Ultem®1000 films in water, the electret behavior was further improved and almost 100% charge retention was achieved. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 1247–1255, 2010

Key words: antioxidants; corona charging; electrets; degradation; high-performance polymers

INTRODUCTION

Ultem®1000 is a commercial polyetherimide (PEI), which was introduced by General Electric (GE) in the early 1970s, and is now part of the portfolio of Sabic Innovative Plastics. The chemical structure of the Ultem®1000 polymer is depicted in Figure 1. This PEI is an amorphous, transparent, amber colored, thermoplastic high-performance polymer and a preferred engineering polymer due to its heat resistance, dimensional stability accompanied by exceptional strength and modulus, and chemical resistance. Krause, Yang, and Sessler found also that Ultem®1000 is a good electret material.[1]

An electret is a dielectric that exhibits a quasi-permanent polarization, which is due to aligned dipoles, surface charges, or injected volume charges.[2,3] Polymer electrets, especially polytetrafluoroethylene (PTFE, Teflon) and its thermoplastic derivative, Teflon-FEP, are widely used as membranes in electret microphones and transducers.[2,4] However, those fluorinated polymers are expensive, in the case of PTFE difficult to process, and yield at higher temperature and stress. Due to these disadvantages and additionally to broaden the applications of electrets, high-temperature polymers are investigated as potential electret materials.

In course of an ongoing research project to identify high-temperature polymer electret materials, we previously reported on the evaluation of several high-performance polymer films, such as PEI, PES, PPS, and PI.[5] For these measurements, exclusively commercial films manufactured by Lipp-Terler (Austria) were used to ensure comparable materials. Based on isothermal potential decay (ITPD) measurements, commercial Ultem®1000 PEI films possessed the best charge storage capability. However, in continuation of this work, we found and reported[6] that films prepared from a PEI synthesized in our lab, with a structure shown in Figure 1 and thus chemically identical to Ultem®1000, exhibited an accelerated charge drain resulting in a poor electret. Thus, we assumed that additives in and/or sizing agents on top of the commercial films might be responsible for the superior charge storage behavior of the Lipp-Terler films.
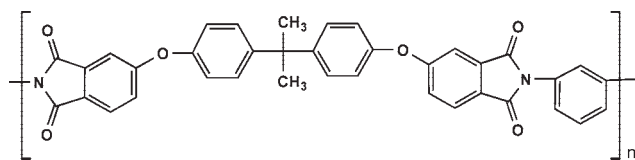
Figure 1 Chemical structure of the Ultem[®]1000 polyetherimide.

Finally, we intend to establish structure-property relationships of PEI and charge retention by investigating the influence of purification, synthetic method, of antioxidants as additives, and of water conditioning on the electret performance of PEI films. To exclude effects of unknown treatments and components used for and in commercial films, we decided to focus on Ultem[®]1000 pellets received directly from GE. Commonly commercial polymers are compounded with an additive package, particularly high-performance polymers which are processed at high temperatures. Depending on the polymer and the final application, the incorporated additives may vary both in amount and species. To shed more light on this matter, we carefully purified the commercial Ultem[®]1000 PEI by reprecipitation and employed ITPD measurements to evaluate the electret performance of compression molded films of this purified PEI. In a further step, we isolated and identified additives in the commercial Ultem[®]1000 material, and melt compounded identical commercial antioxidants into purified PEI to study the effect of these additives on the electret performance.

EXPERIMENTAL SECTION

Materials

Ultem[®]1000 pellets were received from GE Plastics, The Netherlands. For purification, the pellets were dissolved (10 wt %) in dichloromethane or γ-butyro-

lactone, and reprecipitated in a 10fold excess of ethanol. The precipitate was extracted in a Soxhlet solid–liquid extractor with isopropanol for 24 h and dried at 100°C in vacuum. Irgafos[®]P-EPQ and Irgafos[®]126 (Fig. 3) were used as received by Ciba Speciality Chemicals, Lampertheim, Germany. All other chemicals and solvents were purchased from Aldrich and also used as received.

Polymerization

PEIs possessing a chemical structure shown in Figure 1 and comparable molecular weight to Ultem[®]1000 (**1a**, see Table I) were synthesized by two different routes. The polymerization of **2** was carried out in *N,N*-dimethylacetamide (DMAc) according to Liaw et al.,[7] whereas **3** was prepared via a method described by Kuznetsov,[8,9] which was slightly modified. More detailed procedures can be found in a previous publication.[6]

Characterization

As characterizations methods ^{1}H, ^{13}C, and ^{31}P NMR spectra (Bruker AC250), thermogravimetric analysis (Mettler Toledo TGA/SDTA 85; heating rate: 10 K/min, air flow: 50 mL/min), and differential scanning calorimetry (Perkin-Elmer DiamondDSC, 10 K/min, nitrogen flow: 30 mL/min) were employed. Inherent viscosities of polymer solutions were measured in a Schott Ubbelohde viscometer (type I) in a Lauda viscoboy 2 at 25.0°C using a solution of 0.5 g/dL polymer in 1-methyl-2-pyrrolidone (NMP).

Additive incorporation

Twice reprecipitated Ultem[®]1000 denoted as **1c** (Table I) and Irgafos[®]P-EPQ or Irgafos[®]126 were mixed using a conical, corotating, 8 mL mini-twin-screw mixer (Technical University Eindhoven, The

TABLE I
Polymer Purification, Inherent Viscosities, and Thermal Properties of the Investigated PEIs

PEI	Treatment prior to compression molding	η_{inh}[a] (dL/g)	T_g[b] (°C)	$T_{5\%}$[c] (°C)
1a (Ultem[®]1000)	None	0.50	221	535
1b	**1a** reprecipitated from CH_2Cl_2[d]	–	–	–
1c	**1b** reprecipitated from CH_2Cl_2[d]	–	–	–
1d	**1a** reprecipitated from γ-butyrolactone	–	–	–
2	Synthesized, reprecipitated from CH_2Cl_2[e]	0.51	221	534
3	Synthesized, reprecipitated from CH_2Cl_2[e]	0.47	221	535

[a] Viscometry: 0.5 g/dL in NMP at 25°C.
[b] DSC: heating rate 10 K/min; second heating.
[c] TGA: heating rate 10 K/min in air; temperature of 5% weight loss.
[d] Precipitated into ethanol, extracted with isopropanol, and dried at 100°C i. vac.
[e] Synthesized by two different methods (see text), precipitated into ethanol, extracted with isopropanol, and dried at 100°C i. vac.

Netherlands) at 366°C at 60 rpm under nitrogen. Between the feeding of the additive/polymer mixture and the discharge of the extrudate about 15 min elapsed. PEI **1c** without additive was also extruded to produce blank control samples. To obtain batches with decreasing additive content in form of a dilution series, the mixer was not discharged completely, and fresh PEI **1c** was fed to the remaining mixer content. Thus, the 1st run of a series contained the highest additive concentration, whereas the 4th run contained a much lower concentration. The actual additive concentration mentioned in the text was determined by carefully weighing the in- and output of polymer for each run.

Film processing

About 0.5 g of PEI was compression molded at 320°C for 6 min in a Paul-Otto Weber GmbH laboratory press and a pressure of 15 kN was applied after 3 min. Films of 100 ± 10 µm thickness were obtained. Each compression molded film was cleaned with isopropanol, dried at 70°C for 14 h, and stored at ambient conditions for 1 h before charging. A detailed procedure is published elsewhere.[6]

Water conditioning

To study the influence of water, Ultem®1000 (**1a**) films were immersed in deionized water and kept there (a) at 90°C for 30 h, (b) at 80°C for 7 days, or (c) at 23°C for 4 days. After this treatment, the films were dried at 110°C for 14 h. The final water content was determined using a Karl Fischer-Coulometer 684 equipped with a KFThermoprep 832 (Metrohm). About 300 mg of the PEI film samples were heated at 180°C for 30 min with a N_2 flow of 40 mL/min. The reported data are averages of at least three individual measurements, the deviation was 0.05 wt %.

Isothermal surface potential decay (ITPD) measurements

Squares (40×40 mm^2) of the PEI films were mounted onto aluminum plates using conductive double-sided adhesive tape.[6,10–12] Samples were charged at +12.5 kV and a grid voltage of +400 V for 20 s at room temperature (r.t.) using a point-to-plate corona setup. The surface potential of the electret films was measured using an electrostatic voltmeter (Monroe Electrostatic Voltmeter 244 A). The first measurement at r.t. was conducted directly after the corona treatment. To accelerate the charge decay, the samples were kept in an oven at 90°C, and additional measurements were performed after 30, 90, 180, 360, and 1440 min (24 h). For better comparison,

all ITPD data are plotted using normalized values V/V_0, which are obtained by dividing each voltage by the initially applied surface potential of 400 V $\pm$ 10 V. Remaining normalized surface potentials after 24 h at 90°C are denoted as V^{24h}/V_0 in percent. Reported is the average of three independent measurements at nine locations using different films; the standard deviation was always below 5%.

## RESULTS AND DISCUSSION

Polymer sample preparation

To avoid confusion about the different polymer samples used in this study, we introduce numbers for each PEI as shown in Table I. Ultem®1000 which was received as pellets, will be referred to as **1a**. This material was purified in two ways: First, **1a** was dissolved in dichloromethane (CH_2Cl_2) and precipitated into ethanol, extracted with isopropanol, and dried; this PEI is denoted as **1b**.

PEI **1c** was obtained by repeating the same reprecipitation step using **1b**. By reprecipitating **1a** from γ-butyrolactone into ethanol, extracting with isopropanol, and drying, we obtained PEI **1d**. The second solvent was chosen instead of CH_2Cl_2 to eliminate a possibly negative influence of a chlorinated solvent regarding the charge storage behavior.

Additionally, we synthesized PEIs as reference materials according to the structure shown in Figure 1 by two different polymerization methods starting from monomers. PEI **2** was prepared by a conventional two-step synthesis in DMAc using pyridine as catalyst and acetic acid anhydride as dehydrating agent.[6,7] The resulting polymer was purified by reprecipitation from CH_2Cl_2 into ethanol followed by extraction with isopropanol, and exhibited an inherent viscosity η_{inh} in NMP of 0.51 dL/g, which is comparable to the value of **1a** (Table I). The measured glass transition temperature (T_g) of **2** is identical to the T_g of **1a** (221°C). Also weight loss temperatures in air at 5% ($T_{5\%}$) for **2** and **1a**, 534°C and 535°C, respectively, can be considered identical. PEI **3** was synthesized in an one-step one-pot synthesis in molten benzoic acid according to a method developed by Kuznetsov[6,8,9] and purified as described above for **2**. Again η_{inh}, T_g, and $T_{5\%}$ were similar to those of **1a**. Most importantly, no additives are present in the PEI **2** and **3** and a thinkable influence of the synthetic method and reagents on the electret performance can be studied.

Influence of purification on the electret performance

For assessing the electret performance of PEIs **1–3**, films of 100 µm thickness were compression molded
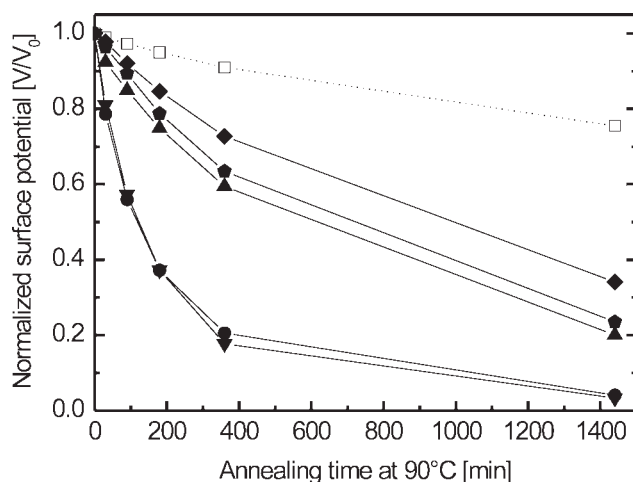
Figure 2 Isothermal surface potential decay (ITPD) curves of compression molded (320°C) and corona-charged films of **1a** (□), **1b** (◆), **1c** (⬟), **1d** (▲), **2** (●), and **3** (▼) after annealing at 90°C.

at 320°C, corona charged at r.t., and the isothermal potential decay (ITPD) at 90°C was determined. More details can be found in the Experimental section and in previous publications.[6,10–12] This accelerated test at elevated temperatures simulates long storage periods at room temperature; for a good electret material, this time might be in the order of decades (see p 191 in Ref. 3).

In Figure 2, the ITPD curves of all investigated PEI films are depicted. For **1a**, the decay behavior has an exponential shape and the remaining surface potential ($V^{24\ h}/V_0$, given in percent) after 24 h of annealing at 90°C was 75% of the initial surface potential. PEI **1b**, which was obtained by reprecipitating **1a** from CH_2Cl_2 into ethanol, shows a distinctly accelerated decay compared with **1a** to $V^{24\ h}/V_0$ of 34%. The charge decay of **1c**, which was reprecipitated twice, is even faster (Fig. 2, curve ⬟) ending at $V^{24\ h}/V_0$ of 24%. Reprecipitation of **1a** was also performed using the nonchlorinated solvent γ-butyrolactone rendering PEI **1d**; for this polymer, the charge decay is even more accelerated than for the twice reprecipitated **1c** and a $V^{24\ h}/V_0$ of only 20% was determined.

Films of the synthesized PEI **2** and **3** exhibit almost identical ITPD curves characterized by very fast charge decay: After 24 h at 90°C almost the entire initial surface potential has vanished (3–4%). This observation implies that the synthetic pathway, namely polymerizing in DMAc/pyridine and acetic acid anhydride as dehydrating agent yielding PEI **2** or polycondensation in molten benzoic acid yielding PEI **3**, has no influence on the overall poor electret performance of **2** and **3**. Consequently, the additive package has a substantial impact on the electret properties, and not the intrinsic chemical structure of the PEI.

Influence of secondary antioxidants as additives on the electret performance

Purification of commercial Ultem®1000 (**1a**) by reprecipitation and extraction will remove low-molecular weight compounds, for instance cyclic and linear oligomers. Also, additives, such as processing aids, plasticizers, antistatics, and most importantly for high-temperature polymers, antioxidants functioning as heat stabilizers, will be removed by purification. Particularly, interesting in the scope of this work, is to chemically identify these extracted compounds since they might function as charge traps and are responsible to improve the electret performance of PEI. The concept of adding additives as charge traps to enhance the charge storage capability was successfully applied for polypropylene.[10,11,13] However, the improvement strongly depends on the additive concentration. The presence of charge traps in commercial Ultem®1000 would explain the better ITPD performance of **1a** (Fig. 2, □) compared with the purified samples **1b-d** (◆, ⬟, ▲).

To identify the postulated charge trap additives in Ultem®1000, the solution remaining after filtering the precipitated PEI was collected, the ethanol evaporated, the residual material further purified, and investigated by spectroscopic methods. Besides PEI oligomers, one majority compound was present, which was characterized by various NMR techniques and elemental analysis. The extracted compound was identified as an organophosphonite. Secondary antioxidants, in this case bulky organophosphorus compounds, are commonly employed as high-temperature heat stabilizers. These P(III) compounds prevent degradation and oxidation of the molten polymer by hydroperoxides and P(V) species are formed during processing. In fact, the ^{31}P, ^{13}C, and ^{1}H NMR spectra of the extracted compound were identical to the antioxidant sold under the trade names Irgafos®P-EPQ (Ciba) and Sandostab®P-EPQ (Clariant), whose structure is depicted in Figure 3(a) (Tetrakis(2,4-di-tert-butylphenyl)[1,1-biphenyl]-4,4′-diylbisphosphonite, CAS number 119345-01-6, taken from Ciba data sheet).[14,15]

Consequently, Irgafos®P-EPQ had to be confirmed in its assumed property as electret performance enhancer. Therefore, this additive was melt compounded with PEI **1c** (reprecipitated and extracted) in a twin-screw mixer at 366°C and batches with different Irgafos®P-EPQ content were prepared. In a first series, an initial additive concentration of 5000 ppm (0.5 wt %, 1st run) Irgafos®P-EPQ was chosen, which was further diluted by adding **1c** yielding load levels of 3200 (2nd run), 2200 (3rd run), 1200 (4th run), and 700 ppm (5th run). PEI **1c** was also extruded to produce a blank control (0 ppm). All
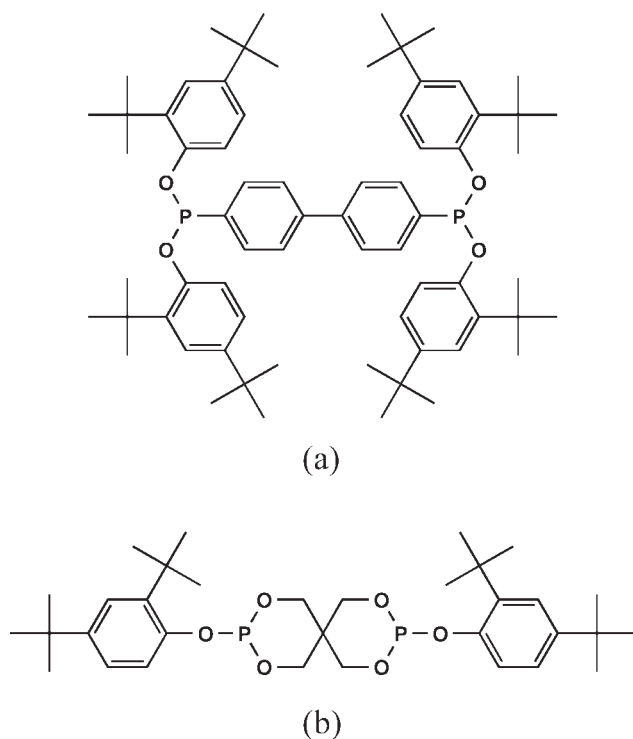
Figure 3 Chemical structures of the organophosphonite (a) sold under the trade names Irgafos®P-EPQ (Ciba) and Sandostab®P-EPQ (Clariant), and of an organophosphite (b) sold under the trademark Irgafos®126 (Ciba).

samples were compression molded at 320°C and the films characterized by ITPD measurements.

Figure 4 shows the ITPD curves of **1c** films with Irgafos®P-EPQ in comparison to a film of **1a**. Comparing the charge decay of **1c** (0 ppm, ⊘) to the one shown in Figure 2 (**1c**, ♠, 34%), the charge drain is even more dramatic: Almost the complete surface potential is depleted within 24 h at 90°C, which we attributed to excessive thermal degradation during the mixing process at 366°C due to the absence of antioxidants.

Additivation with Irgafos®P-EPQ clearly improves the charge storage capability of **1c**. A pronounced improvement of the electret performance with increasing additive level was found. Films with the highest concentration of 5000 ppm (Fig. 4, ◆) Irgafos®P-EPQ exhibit a surface potential ($V^{24 h}/V_0$) of 79%, which is slightly better than the retention for **1a** (commercial Ultem®1000) films (□, 75%). Films with lower additive concentrations of 3200 ppm (♠), 2200 ppm (▲), and 1200 ppm (●) show decay curves with very similar remaining surface potentials ($V^{24 h}/V_0$) of 52–55%. These results suggest that in this concentration range, a surface potential plateau is formed, wherein the ratio of oxidized P(V) and phosphonite P(III) is balanced and thus the electret performance is dominated more by the organophosphite acting as charge trap and not by thermal

degradation products. At the lowest concentration of 700 ppm (▼), the film exhibited a charge retention ($V^{24 h}/V_0$) of only 25%, which is still distinctly better than purified PEI **1c** (⊘, 3%). However, the long residence time of the 700 ppm Irgafos®P-EPQ batch in the mixer due to the diluting procedure may promote thermal degradation and thus charge drain is accelerated for this low concentration.

Therefore, in a second series, **1c** was compounded again with Irgafos®P-EPQ but at lower loading levels starting at an additive concentration of 500 ppm (1st run). Dilution yielded batches with 250 (2nd run), 160 (3rd run), and 100 ppm (4th run) of Irgafos®P-EPQ. In Figure 5, the resulting ITPD curves of the charged films are displayed. The curve of the blank run (**1c**, 0 ppm, ⊘) without any additive and the data for films of commercial Ultem®1000 (**1a**, □) are also displayed.

In this second series, $V^{24 h}/V_0$ ratios show a correlation with the additive concentration and the remaining surface potential decreases with lower load level. Films with the highest concentration of 500 ppm (Fig. 5, ◆) Irgafos®P-EPQ resulted in $V^{24 h}/V_0 = 63\%$ charge retention, which is slightly lower that the value (75%) of the **1a** films (commercial Ultem®1000). This batch had also the shortest residence time in the mixer. The electret performance of this 500 ppm film of the second series (63%) excels those of the first series of **1c** (700 ppm; Fig. 4, $V^{24 h}/V_0 = 25\%$). However, parts of the batch with 700 ppm (1st series, 5th run) stayed much longer in the mixer than the 500 ppm-batch (2nd series, 1st run). These results show that besides the additive concentration, the residence time in the mixer and
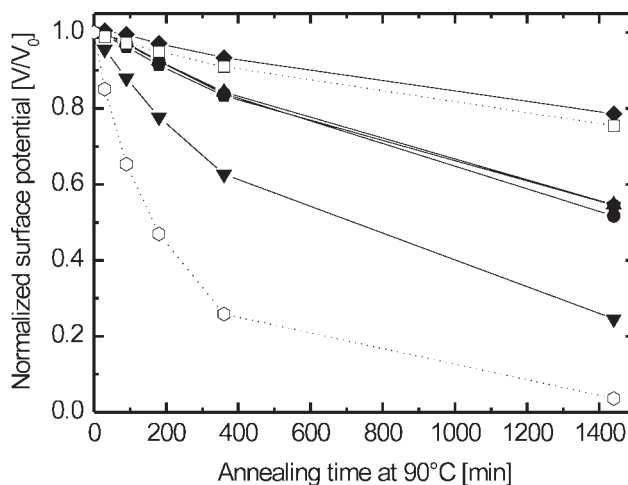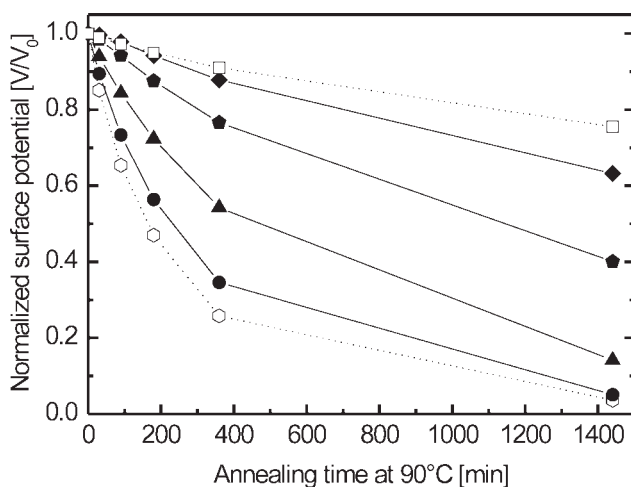

Figure 4 Isothermal surface potential decay (ITPD) curves of melt compounded (366°C), compression molded (320°C), and corona-charged films of **1c** additivated with 5000 (◆), 3200 (♠), 2200 (▲), 1200 (●), 700 (▼), and 0 ppm (□) Irgafos®P-EPQ. For comparison the curve for **1a** (□) is also included.

thus the degree of thermal degradation has an additional impact on the electret behavior. Hence, PEI degradation products promote charge drain and thus are detrimental for the overall electret performance; this will be discussed in more detail later. Attempts to avoid thermal degradation by employing solution cast films were unsuccessful due to traces of remaining solvent and insufficient film quality, thus inflicting ITPD measurements.

The mechanism of Irgafos®P-EPQ as secondary antioxidant is based on the oxidation of phosphonite P(III) to phosphonate P(V). Based on the dramatic charge drain of thermally stressed PEI samples, we conclude that only the original phosphonite P(III) species is capable of acting as charge trap in PEI and not the oxidized P(V) derivative. Consequently, the added Irgafos®P-EPQ acts in two ways, by suppressing thermal degradation, which itself accelerates charge decay, and as a charge trap.

To assess the scope of commercial secondary antioxidants as electret enhancers, we selected another P(III) compound as additive for PEI. Irgafos®126 (Bis-(2,4-di-t-butylphenol)pentaerythritol diphosphite, CAS number 26741-53-7, taken from Ciba data sheet.),[14-16] [Fig. 3(b)] is known as organophosphite which is oxidized during heat stabilization forming organophosphates. Irgafos®126 was melt compounded with 1c in the same way as described above for Irgafos®P-EPQ. Electret films with concentrations of 5000 ppm, 3200 ppm, and 1200 ppm were subjected to ITPD measurements, the corresponding data are displayed in Figure 6. Films of 1c additivated with 5000 ppm Irgafos®126 (◆) exhibited a remain-
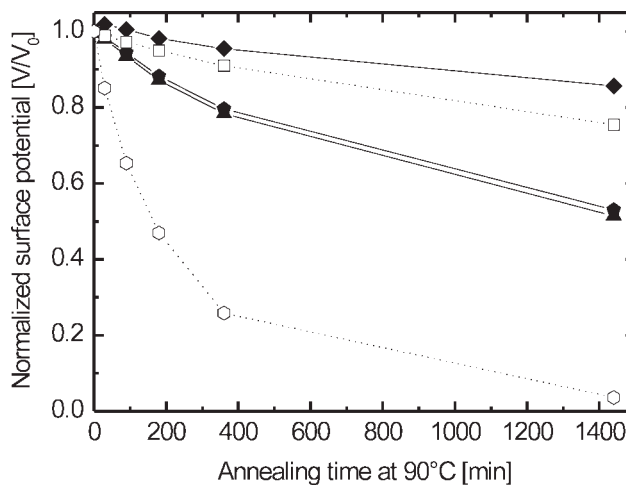
Figure 6 Isothermal surface potential decay (ITPD) curves of melt compounded (366°C), compression molded (320°C), and corona-charged films of reprecipitated **1c** additivated with 5000 (◆), 3200 (⬠), 1200 (▲), and 0 ppm (○) Irgafos®126. For comparison, the ITPD of **1a** (□) is also included.

ing surface potential ($V^{24\,h}/V_0$) of 86% and therefore is clearly above the electret performance of **1a** (□, 75%). The ITPD curves obtained with films containing 3200 ppm (⬠) and 1200 ppm (▲) are of very similar shape resulting in a $V^{24\,h}/V_0$ of 51% and 53%, respectively. In summary, at comparable load levels, films containing Irgafos®126 are better electret materials than films containing Irgafos®P-EPQ. These result are in agreement with the fact that Irgafos®126 is a more efficient antioxidant than Irgafos®P-EPQ.[14]

Influence of water conditioning on the electret performance

As mentioned before, thermal degradation products formed during melt processing are detrimental for the overall electret performance. To further purify the melt compressed films, we conditioned the films by immersing in water for different times and temperatures.

Thus, individual compression molded films of commercial Ultem®1000 (**1a**) were immersed in deionized water for 30 h at 90°C, for 7 days at 80°C, and for 4 days at 23°C. To provide comparable conditions before charging, all soaked films were dried at 110°C for 14 h without vacuum and equilibrated at ambient atmosphere and temperature for 1 h before corona charging. This treatment was necessary since on one hand it was practically impossible to charge films reproducibly without this equilibration step and on the other hand this reflects much more conditions encountered in a future application. The water content of all films was monitored by Karl-Fischer measurements. Compression molded films of **1a** revealed a

Figure 5 Isothermal surface potential decay (ITPD) curves of melt compounded (366°C), compression molded (320°C), and corona-charged films of reprecipitated **1c** additivated with 500 (◆), 250 (⬠), 160 (▲), 100 (●), and 0 ppm (○) Irgafos®P-EPQ. For comparison, the ITPD of **1a** (□) is also included.

water content of 0.50 wt %, whereas compression molded, immersed, and subsequently dried films of **1a** exhibited 0.46 wt %. The almost identical values indicate that the films very quickly absorb water upto this value during equilibration step.

Figure 7(a) depicts the ITPD curves of the films stored in water, where Figure 7(b) shows a more detailed view of the initial phase of the ITPD curves. Surprisingly, all films stored in water exhibit a distinctly better charge storage capability than untreated **1a** films. Films immersed in water at 80°C for 7 days (◆) and dried maintain almost their initial surface potential of $V^{24\ h}/V_0 = 98\%$. A shorter immersion time in combination with a lower temperature, more precisely 4 days at 23°C (▲), rendered electrets which kept a $V^{24\ h}/V_0$ of 94%. Also an excellent electret (97%) are films, which were immersed in water for a shorter period of time, but at a higher temperature (30 h, 90°C; ⬟).

We first assumed that a treatment with water would hydrolyze the organophosphites and -phosphonites and thus destroy the charge traps. Moreover, the formed polar hydrolysis products should further accelerate the surface potential decay but the observed results contradict these assumptions.

Both secondary antioxidants, phosphonite (Irgafos®P-EPQ) and phosphite (Irgafos®126), are sensitive to water, the hydrolysis mechanism and products are well documented in the Refs. [15,16–19]. Based on these references, hydrolysis leads to substituted phenols, polyvalent alcohols, and phosphorous acid. At this pH (neutral) water induced hydrolysis of the PEI backbone is unlikely and negligible.[20]

The thermal oxidation processes during the degradation of PEI have been intensively studied by Carroccio et al.[21] On the basis of mass spectrometry, they found a variety of fragments, i.e., acetophenone, phenylacetic acid, phenols, benzoic acid, bisphenol A, among others.

Without doubt, all polar compounds and fragments mentioned so far have the potential to accelerate the charge decay in electret materials dramatically. It is also feasible that during the storage in water, these polar compounds are removed or diminished by diffusion into the water phase, and this process is most efficiently using hot water. As mentioned before, after the treatment with water, all films were dried at 110°C for 14 h and equilibrated to a final water content of about 0.5 wt %. Hence, the water content in the films is virtually the same and obviously this water does not inflict the electret performance. This could be explained by a strong water molecule immobilization by the carbonyl groups, which is well documented for polyimides[22-24] and also for PEI.[20,25,26] Consequently, by immersing the samples in water, hydrophilic low-molecular mass fragments and compounds, which are notori-
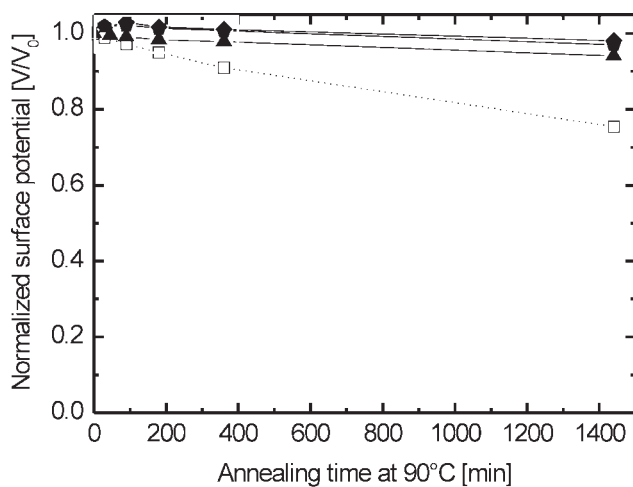
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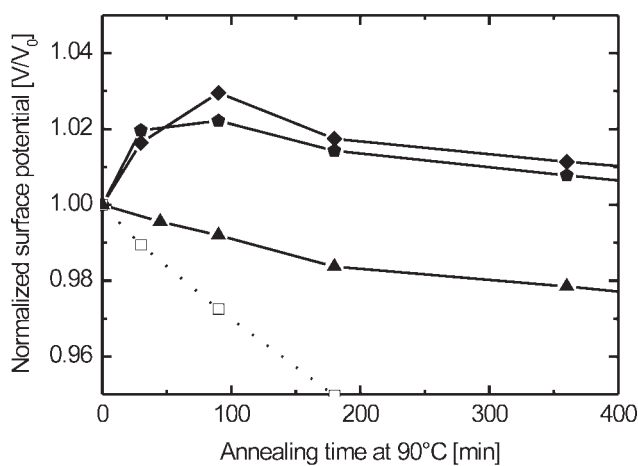
(b)

Figure 7 (a) Isothermal surface potential decay (ITPD) curves of compression molded (320°C) films **1a** (commercial Ultem®1000), which were immersed in water at 90°C for 30 h (⬟), at 80°C for 7 days (◆), and at 23°C for 4 days (▲) previously to drying and corona-charging. For comparison, the curve for untreated compression molded **1a** films (□) is also included. (b) Magnified graph of the insert shown in (a). Identical ITPD curves, but as magnified view of initial phase of the charge decay. Clearly, the increase of surface potential up to 103% is visible in the films immersed at 80°C for 7 days (◆) and at 90°C for 30 h (⬟).

ous charge carriers, were removed by a process similar to an extraction.

In addition to the excellent charge retention, the ITPD curves of the films immersed in water at 80°C and 90°C [see magnified view of Fig. 7(b); ◆ and ⬟] show a maximum after 90 min of annealing at 90°C, indicated by a relative surface potential $V^{90\ min}/V_0$ of 103% and 102%, respectively. This maximum is reproducible and not an artifact. The increase of the surface potential is documented in the Refs. 27,28 and is due to the coexistent presence of hetero- and

homocharges. Briefly summarized, surface charges with same sign than the corona electrode are called homocharges and are real charges.[2] Heterocharges, however, are linked to dielectric absorption involving dipoles or ionic charges and are aligned opposite to the applied electric field during charging and afterward to the field generated by surface charges. The observed initial increase in net homocharge is due to the decay of the heterocharge and is just what one would expect if both heterocharges and homocharges are present in a net homocharge sample.[27] Generally, only in very stable corona-charged polymer electrets containing dipoles, this initial increase in the ITPD curve can be observed due to heterocharges. If heterocharges are absent, this effect is not observed. For less stable polymer electrets, this increase in V/V_0 compensated by a much faster charge drain, resulting in the usually observed drop in V/V_0 even after short annealing times.

SUMMARY AND CONCLUSIONS

In this contribution, we investigated the influence of antioxidants as additives on the electret performance of Ultem®1000 polyetherimide (PEI). First, we purified commercial PEI pellets by reprecipitation, then isolated and identified incorporated substances as antioxidants based on phosphonite and phosphite chemistry. In a second step, we melt compounded commercial antioxidants (Iragfos®P-EPQ, Irgafos®126) into purified PEI to systematically investigate the effect of these additives on the electret performance as function of the additive load level. Films of the compounds were melt compressed and their electret performance evaluated by isothermal potential decay measurements (ITPD).

Purified and synthesized PEIs are poor electrets, with charge retentions of 34% and almost 0% after 24 h at 90°C, respectively, compared with 75% of the unpurified PEI. However, the charge capability can be improved dramatically by secondary antioxidants. For instance, after adding 5000 ppm of Irgafos®126 to the purified PEI a charge retention of 86% was determined. We interpret these results that the additive acts as a charge trap, and/or the additive is very effective in reducing species generated by thermal oxidation which promote charge drift.

The charge storage capability of Ultem®1000 films was also greatly improved by immersing the films in water for longer periods. Films which were stored in water at 80°C for 7 days maintained 98% of the initially applied surface potential after 24 h at 90°C. This can be explained by diffusion, and thus removal of polar hydrolysis and degradation products of the additive and the polymer, respectively, from the film by extraction with water.

In conclusion, the charge storage capability of PEI films, and certainly that holds true for most polymers, depends on many factors, such as chemical structure, charging conditions, and application temperature. In course of this work, we were able to shown that also other factors, such as polymer grade, processing conditions, and additive package, have a major impact on the charge storage performance of PEI. If this is taken into consideration, it is possible to achieve excellent electret materials based on polyetherimides.

This work also demonstrates that ITPD measurements on corona-charged polymer films is an extremely sensitive method to determine even little variations in chemical structure, purity, additive content, and quality of the film, which cannot be detected easily by other characterization methods.

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