

Electret Properties of Polyethylene and Polytetrafluoroethylene Films with Chemically Modified Surface

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ABSTRACT

This paper investigates the effect of chemical surface modification of polytetrafluoroethylene (PTFE) and low density polyethylene (LDPE) films on their electret properties. PTFE films were subjected to wet treatment with three different chemicals: orthophosphoric acid, tetrabutyl titanate and tetraethoxysilane. The technique based on the principles of molecular layer deposition (MLD) method was used to modify the surface of LDPE films with phosphorus trichloride vapors. The surfaces of the films were then corona charged, and the electret charge stability was studied by means of isothermal and thermally stimulated surface potential decay. Both PTFE and LDPE films, after the surface treatment, displayed a considerable enhancement in the charge stability compared to the virgin samples. It is important to note that the enhancement of the charge stability was achieved in the positively charged PTFE films, a result important to practical applications. We attribute this effect of charge stabilization to the formation of new energetically deep traps on the modified surface. Decrease in molecular mobility, due to attachment of new chemical structures to the surface macromolecules, may also contribute to the overall growth of the charge stability.

Index Terms — Electrets, surface treatment, charge stability, charge carrier processes, polytetrafluoroethylene, polyethylene.

1 INTRODUCTION

THE electret effect, as well as related phenomena of charge storage and transport, continue to be the focus of research for many investigators [1-11]. A special emphasis is put on the investigation of the charge stabilization mechanisms in polymers. The later is to be expected, as charge stability is absolutely critical for the practical application of polymer electrets. Electret materials with high stability of charge are in demand not only in such a well known areas as electro acoustics, filtration and sensors production [1], but also in the relatively new and developing field of ferroelectrets [12-15]. The stability of piezoelectric coefficients in these voided materials is largely dependent on the charge stability [14, 16].

Among various known methods to increase the electret charge stability, two separate groups or approaches can be discerned.

The first group includes charge stabilization methods based on the optimization of the process of charging. For example, this can be achieved by means of proper technique or regime of charging (corona, electron beam, liquid contact and so on) [1, 4, 12, 19, 20]. To the same group also belong well known methods of thermal stabilization of charge [1, 4, 17, 18]. Here, in the course of heating during poling, the shallow traps are being emptied while the deeper traps still retain charges after subsequent rapid cooling.

In the second group there are charge stabilization methods based on the physical and chemical modification of polymers. These include stretching [10, 12, 21, 22], various thermal treatments (tempering, quenching) [20], incorporation of different additives into the polymer matrix [10, 11], doping [22], chemical grafting of functional groups [23-26,]. For example, recently in [11] it has been shown that the incorporation of the range of additives into the bulk of polypropylene leads (at certain concentrations) to considerable improvement of the electret properties.

In principle, to the second group of the charge stabilization methods also belongs liquid and gas-phase chemical modification of polymer surface [23, 25-27]. The distinctive feature of these methods is that they affect only the surface of the polymer as opposed to the methods discussed above. That is why surface modification can be an efficient tool for charge stabilization if the electret charge storage and relaxation are mostly determined by the surface traps. Later is typical of polytetrafluoroethylene (PTFE) films poled in positive corona [4]. For example, in [25] it has been found that the treatment of PTFE films with phosphorus trichloride vapors leads to the formation of energetically deep traps related to the phosphorus-containing nanosized groups on the surface. As a result, the stability of the positive homocharge was considerably improved. Recently similar results have been obtained for low density polyethylene (LDPE) films [26] and fibrous mats [28], poled in negative and positive corona. It must be noted, however, that when a chemical treatment is applied to the surface of the polymer, due to diffusion, porosity and migration of defects, modification occurs in certain surface layer. Determination of the depth of this layer is a both technically and scientifically challenging task. In this paper, the term surface is referred to a thin surface layer which thickness is small, compared to the film thickness.

In the present work the influence of chemical modification of the polymer's surface on electret properties has been investigated. Two commercially important polymeric materials were studied, namely polytetrafluoroethylene and low density polyethylene. LDPE films were subjected to gas-phase modification (treatment with phosphorus trichloride vapors) whereas PTFE films were liquid-phase modified with orthophosphoric acid, tetrabutyl titanate and tetraethoxysilane.

2 EXPERIMENTAL

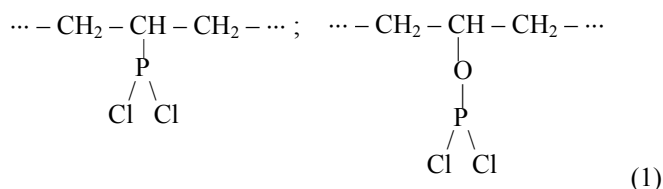
2.1 SAMPLES PREPARATION

The initial materials for the investigation were low density polyethylene (LDPE) films with the thickness of 120 μm (AO Plastpolymer, Russia), 25 μm thick LDPE films (Goodfellow Cambridge, England) and polytetrafluoroethylene (PTFE) films with the thickness of 13 μm (AO Plastpolymer, Russia).

The surface of LDPE films was modified with phosphorus trichloride (PCl_3) vapors. A detailed description of the flow reactor used for this purpose is presented in [28]. The synthesis of phosphorus-containing nanostructures on LDPE surface was carried out at the temperature of 60°C for 10 minutes. The completion of reactions on the modified surface was ascertained by the cessation of the HCl emission at the reactor outlet. Then the films were heat-pressed onto the aluminum foil substrate which acted as an electrode. During the heat pressing at the temperature of 130 °C, the pressure of 0.2 MPa was maintained for 120 s with the subsequent cooling down to the room temperature. LDPE-Al structures based on the non-modified polymer films were fabricated in the same manner.

In [26] physical, chemical, and structural properties of the modified LDPE samples were studied by means of infrared

spectroscopy, atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). It has been found that the concentration of phosphorus on modified LDPE surface was 3.5 at%, whereas chemical analysis of the samples showed the total concentration of phosphorus to be about 0.4 wt%. This fact gives clear indication that only a thin surface layer of the polymer was modified. It was proposed that the modifying reagent chemically interacts with the surface of the polymer, forming the following nanosized groups:



According to AFM data [26] these groups build up "island" structures of 80-200 nm in diameter with the height of 16-20 nm. Surface concentration of these "islands" is approximately 20-25 μm^{-2} . It must be noted that

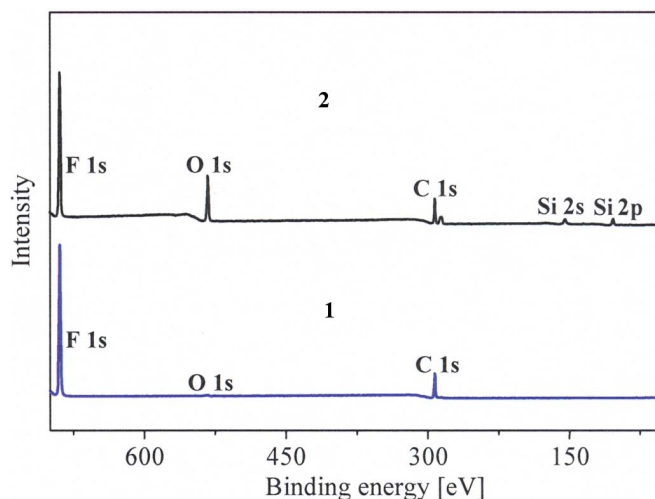


Figure 1. Wide scan XPS spectra of PTFE surface: 1 – virgin sample; 2 – sample treated with tetraethoxysilane. Curve 2 is shifted upwards for better visibility. Intensities for both curves are normalized with respect to maximum value.

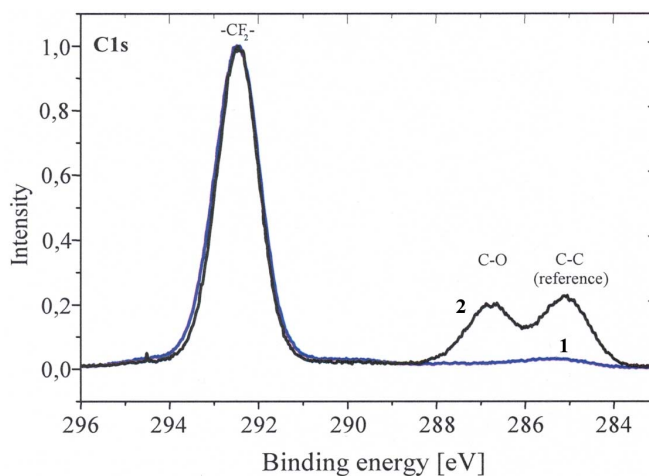


Figure 2. High-resolution C1s XPS spectra of PTFE surface: 1 – virgin sample; 2 – sample treated with tetraethoxysilane.

Table 1. Chemical composition of PTFE surface (wide scan).

| Sample | C in at% | O in at% | F in at% | Si in at% |
|----------|----------|----------|----------|-----------|
| Modified | 32,1 | 17,0 | 44,7 | 6,2 |
| Virgin | 32,4 | 0,5 | 67,1 | <0,02 |

Table 2. Chemical composition of PTFE surface (detailed C1s).

| Sample | CF ₂ in C% | C-C in C% | C-O in C% | CF ₃ in C% | CF in C% | rest in C% |
|----------|-----------------------|-----------|-----------|-----------------------|----------|------------|
| Modified | 66,8 | 16,0 | 13,7 | 1,4 | 0,7 | 1,4 |
| Virgin | 87,6 | 2,6 | 1,4 | 3,8 | 1,0 | 3,6 |

the interaction of the modified surface with the atmospheric moisture can result in the substitution of chloride ions with hydroxyl groups.

The surface of PTFE films was modified using liquid reagents. Prior to modification an aluminum electrode was deposited on one side of the films. Three different reagents were used for surface modification: 60% orthophosphoric acid (H₃PO₄), tetrabutyl titanate (Ti(-O-CH₂-CH₂-CH₂-CH₃)₄) and tetraethoxysilane (Si(-O-CH₂-CH₃)₄). Surface treatment of PTFE material was carried out at room temperature by means of direct contact of the non-metalized side of the film with the respective liquid. The exposure time was 1 hour. Then the excess reagents were rinsed out with water and the films were dried in the air at the temperature of 60 °C.

As a result of such a treatment the chemical composition of the polymer surface is considerably altered. As an example the wide scan XPS spectra of the PTFE samples modified with tetraethoxysilane are shown in Figure 1. The high-resolution C1s spectra are presented in Figure 2. All the information on chemical composition of PTFE surface prior and after the treatment with tetraethoxysilane is summarized in Tables 1 and 2. The experimental data clearly indicates that the liquid treatment with tetraethoxysilane results in defluorination and oxidation of PTFE surface. The concentration of silicon on the modified surface was found to be 6.2 at%.

2.2 ELECTRET MEASUREMENTS

The electret state in both LDPE and PTFE films was formed via electrization in positive corona discharge at room temperature for 30 s. The corona setup with needle electrode was used. The setup was equipped with the control grid electrode, making it possible to obtain samples with a preset initial surface potential value V_0 .

Electret homocharge stability was studied by means of isothermal (ITSPD) and thermally stimulated (TSSPD) surface potential decay techniques. In both cases the surface potential of electrets was measured by noncontact dynamic capacitor method [1]. The experimental setup ("Electret-2009M" Institute of Physics, Herzen University) provided sample temperature control in both isothermal and linear heating regimes. In the thermally stimulated measurements the heating rate was 5 °C/min. The isothermal measurements were carried out at temperatures of 60 °C and 80 °C.

3 EXPERIMENTAL RESULTS AND DISCUSSION

3.1 POLYETHYLENE FILMS

The experimental results of thermally stimulated surface potential decay in the LDPE films (produced by AO "Plastpolymer") charged in positive corona are shown in Figure 3. The virgin samples (curves 1 and 2) clearly show the "crossover" phenomenon. Curve 1 for the sample with higher initial value of surface potential ($V_0=+1780V$) crosses the curve 2 corresponding to the sample with lower initial surface potential ($V_0=+520V$). This phenomenon was frequently observed for LDPE electrets. There are several models that explain it [5, 6, 7, 29, 31]. For example, the "crossover" phenomenon can be due to the existence of the surface traps energetically deeper than those in the bulk of the polymer. As the initial surface potential increases so does the charge injection from the surface into the bulk (for example by means of mechanism of field-dependent injection efficiency, described in [31]). This leads to faster potential decay in the samples with the higher V_0 . TSSPD data for LDPE films modified with phosphorus trichloride vapors (Figure 3, curves 3 and 4) argue in favor of this model. The homocharge stability in these films is considerably higher than that in the virgin samples. For example, the half-value temperature (that temperature at which the surface potential decays to one-half of its initial value during heating) is increased by 55 °C in modified samples compared to virgin ones (compare curves 1 and 3). It is important to note that the "crossover" phenomenon can no longer be observed in modified samples (curves 3 and 4).

We believe that this result has a considerable practical value for electret devices, since surface modification not only increases the charge stability but also the magnitude of the stabilized charge. Practically, the electrets made from modified LDPE films can compete with the electrets based on isotactic polypropylene [23]. Similar results were obtained in chemically modified LDPE films charged in negative corona (not shown here) [26].

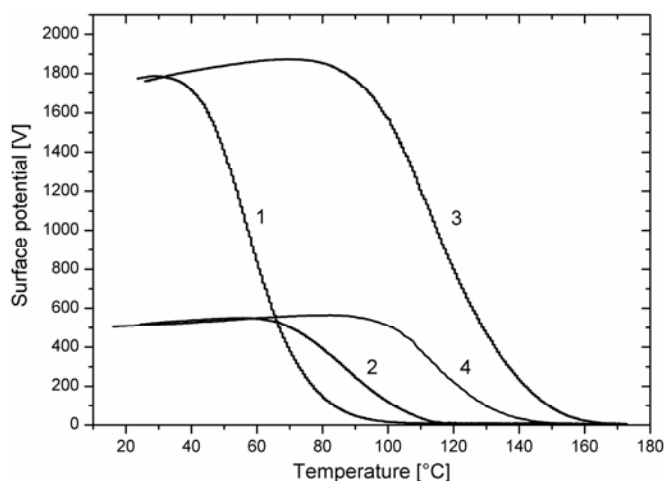


Figure 3. Thermally stimulated surface potential decay in positively charged LDPE films (AO Plastpolymer): 1,2 – virgin samples; 3,4 – samples treated with phosphorus trichloride vapors.

The observed phenomenon of charge stabilization we attribute to the formation of phosphorus-containing groups (1). These structures can act as energetically deep traps capable of long storage of the electret homocharge. Indeed, calculations in [9, 32] show that the traps, related to the chemical defects and impurities in model polyethylene structures, are deeper compared to those of physical nature. It was, however, noted that the concentration of traps related to non-stoichiometric defects is quite low (approximately 500 times lower than the concentration of “physical” traps). Yet, it must be taken into consideration that the concentration of non-stoichiometric defects on the surfaces of real polymers can be appreciably higher than in the bulk. Some indication of this difference in concentrations can be obtained from XPS data for PTFE films (Tables 1 and 2). There the polymer surface, brought to contact with suitable environment, experience a one order of magnitude change in concentration of chemical defects.

In the process of poling, charges are captured on both initial shallow and new deep traps on the polymer surface (or rather in the thin surface layer). When the charges escape shallow traps they move a short distance laterally or transversally to be trapped on a nearest new deep trap. That means that decay features of the initial shallow traps of the virgin sample, cannot be observed in the decay curves of the modified sample. Data shown in Figure 3 support this assumption.

The decrease in molecular mobility on LDPE surface treated with phosphorus trichloride vapors can be yet another reason for the improvement of the electret charge stability. The massive phosphorus-containing structures can provide steric hindrance for the micro-Brownian motion of the surface macromolecules. Besides, such structures, having a dipole moment, facilitate intermolecular interactions. All these factors reduce the probability of thermal activation of charges from the surface traps (by means of reducing the frequency factor). In favor of such a mechanism argues the fact that even at temperatures above crystallites melting point (109-110 °C) there is still an appreciable fraction of charge on the modified

surface. Complete discharging takes place at temperatures above 150 °C.

Thus, the formation of deep traps on the surface of LDPE has an immediate effect on electret properties of this material. Not only the thermal stability of the electret charge is enhanced but also the magnitude of the surface charge density can be increased. The latter is possible because of the elimination of the “crossover” phenomenon. Indeed, during poling, charges will preferably be trapped on the new deep surface traps. This will reduce injection and trapping on the shallow bulk traps, thus eliminating the “crossover” phenomenon.

The charge decay in electrets can be determined not only by the activation of charges from the corona charged surface but also be due to the movement of charges injected from the rear electrode [5-7]. In our experiments both surfaces of LDPE film were treated with PCl_3 vapors prior to the deposition of the electrode. That is why, in case of charge injection from the electrode, these charges cannot partake in transport across the film, being held by the deep traps on the modified surface.

It is known that the properties (including electret ones) of the same polymer are dependent on the production technology and can vary substantially with different producers. Therefore we investigated the same phenomenon of charge stabilization in LDPE films supplied by different vendor (Goodfellow Cambridge). The experimental results are presented in Figure 4. Obviously, the charge stability in the virgin sample (curve 1) is extremely low. Charge decay in such samples begins already in the process of poling. In the thermally stimulated regime only the final stages of the surface potential decay can be registered. According to the concepts discussed above, this result suggests that the surface of the virgin films contains very few of the non-stoichiometric defects. However, after the treatment with PCl_3 vapors, the charge stability has been considerably enhanced. Thus, the half-value temperature has increased by 71 °C in the modified samples compared to virgin ones (curves 1 and 2). As with Plastpolymer films, the “crossover” phenomenon is not observed in the modified samples (curves 2 and 3).

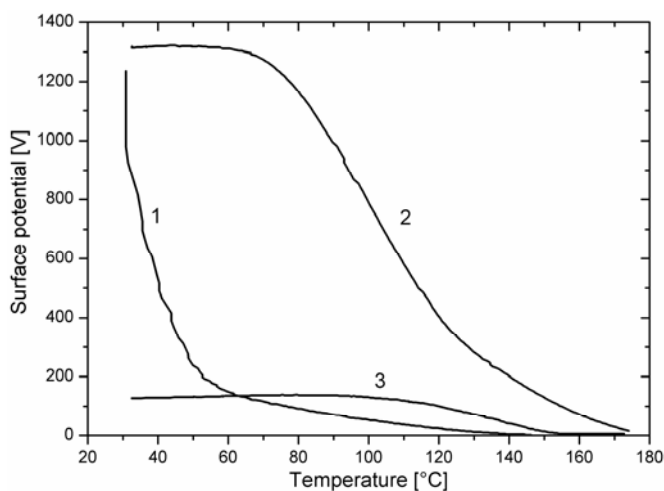


Figure 4. Thermally stimulated surface potential decay in positively charged LDPE films (Goodfellow): 1 – virgin sample; 2,3 – samples treated with phosphorus trichloride vapors.

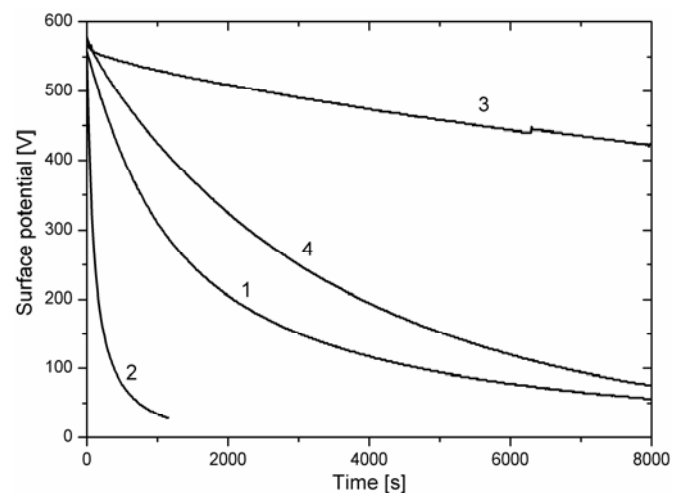


Figure 5. Isothermal surface potential decay in positively charged LDPE films (Plastpolymer): 1 – virgin sample, 60°C; 2 – virgin sample, 80°C; 3 – treated with PCl_3 vapors, 60°C; 4 – treated with PCl_3 vapors, 80°C.

In Figure 5 the isothermal surface potential decay in LDPE films (Plastpolymer) is shown. In this experiment the surface potentials were measured continuously at elevated temperatures. These data are in a good agreement with the thermally stimulated decay results. Time stability of charge in the modified films (curves 3 and 4) is considerably higher than in the virgin samples (curves 1 and 2). Thus, the chemical modification of the surface of LDPE films is an efficient method to enhance the electret properties of this material.

3.2 POLYTETRAFLUOROETHYLENE FILMS

It is widely known [1, 4, 23] that PTFE films, charged in negative corona, possess an exceptionally high stability of the electret charge. On the other hand, charging in the positive corona yields appreciably less stable electrets. For the PTFE films studied in the present paper this can be easily seen when curves 1 and 5 in the Figure 6 are compared. In [23, 27] apparently for the first time the long-lived positive electrets were obtained by means of wet chemical modification of PTFE surface. In the present paper we employ similar approach to the positive charge stabilization in PTFE. Here we use orthophosphoric acid, silicon- and titanium-containing reagents for surface modification.

Figure 6 shows the thermally stimulated surface potential decay in both virgin and wet treated PTFE films. Here and below all curves are normalized with respect to the initial value of surface potential ($V_0=+500V$). Chemical treatment of PTFE surface results in considerable enhancement of thermal stability of the electret charge. The shift of the experimental curves to the higher temperature region is determined by the chemical nature of the modifying reagent. The thermal stability of positive charge increases within the range of chemicals used, starting with tetraethoxysilane (curve 2), then tetrabutyl titanate (curve 3), and the best results are obtained with orthophosphoric acid treatment. It was found, however,

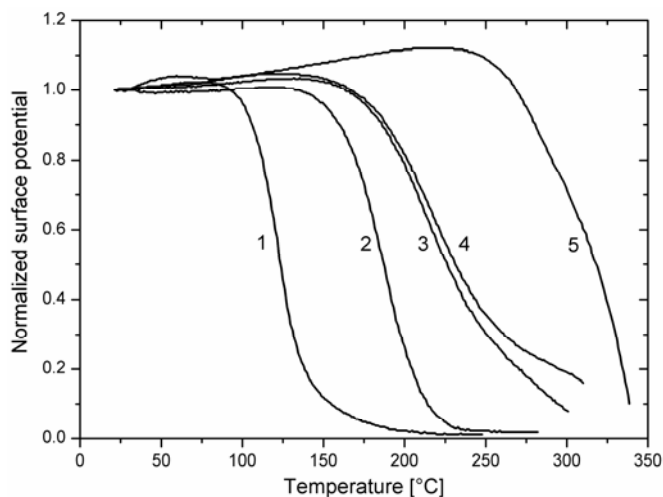


Figure 6. Thermally stimulated surface potential decay in PTFE films positively (1,2,3,4) and negatively (5) charged; 1,5 – virgin samples; 2 – sample treated with tetraethoxysilane; 3 – sample treated with tetrabutyl titanate; 4 – sample treated with orthophosphoric acid.

that these treatments do not affect the stability of negative charge, so the curve 5 is also valid for the negatively charged modified samples.

The results obtained can be interpreted as follows. It is known [4, 23] that in non-polar fluoropolymers the positive homocharge relaxation is largely limited by the processes of charge activation from the surface traps. The charge carriers, after being released from the surface traps, drift through the volume of the sample in the regime of continuous retrapping. Their time-of-flight, however, is much shorter than their lifetime in the surface traps. As a result, the derivative of the TSSPD signal with respect to temperature (after the proper axis transformation) directly represents the energy spectrum of these traps [4]. That is why we relate the phenomenon of charge stabilization by means of surface treatment to the formation of new groups of energetically deep traps. These can be the functional groups formed via interaction of modifying reagents with the non-stoichiometric defects on the surface. For example, the XPS data shown in 2.1 suggest that the treatment with tetraethoxysilane result in defluorination and oxidation of the surface and $-O-Si(OH_3)$ groups are attached to the main carbon chain. Besides, on the modified surface there are OH groups that substitute fluorine atoms. As it has been suggested above for LDPE films, the decrease in the molecular mobility on the modified surface can also contribute to the charge stabilization. For instance, in [25] it has been shown that surface modification of PTFE with phosphorus trichloride vapors cause the frequency factor (an attempt to escape frequency) of the surface traps to decrease from $7 \cdot 10^{13} s^{-1}$ down to $6 \cdot 10^{12} s^{-1}$. This experimental fact can serve as an indirect proof of the proposed decrease in the molecular mobility on the modified surface.

It is possible that in the course of liquid treatment not all the adsorbed molecules of modifying reagents build sufficiently strong chemical bonds with the surface macromolecules. It is of interest, therefore, to investigate the influence of thermal treatment on the electret properties of chemically modified PTFE films.

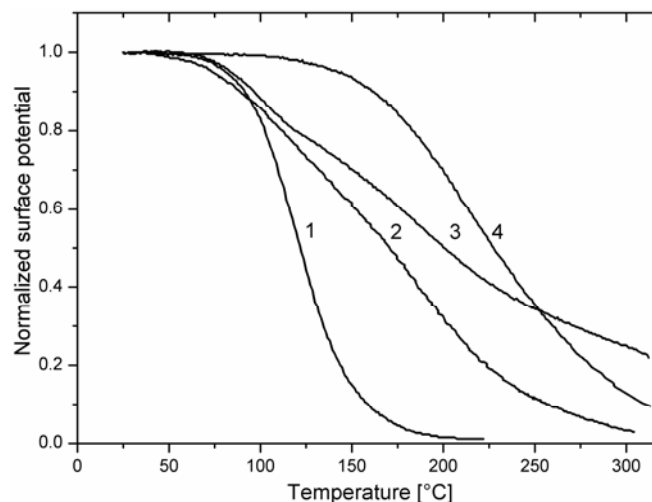


Figure 7. The influence of thermal treatment of the modified PTFE films on thermally stimulated surface potential decay: 1 – virgin sample; 2 – sample treated with tetrabutyl titanate; 3 – sample treated with orthophosphoric acid; 4 – sample treated with tetraethoxysilane.

When the investigations were planned, it was supposed that the combined treatment, which includes chemical modification with subsequent heating, may result in two alternative outcomes. First one is the desorption of at least a fraction of the modifying reagent molecules. Conversely, the second outcome is the enhancement of chemical reactions that leads to the increase in the number of trapping sites on the surface. Based on these considerations we chose the temperature for the thermal treatment to be 305-310 °C i.e. in the vicinity of the crystallites melting point (327 °C) in PTFE. In this temperature range the mobility of macromolecules in the amorphous and crystalline regions increases rapidly, stimulating the processes discussed above.

The results of thermally stimulated potential decay experiments are presented in Figure 7. Obviously the thermal treatment has a considerable effect on the electret properties of modified samples (curves 2, 3, and 4), whereas TSSPD of non-modified films is practically unchanged (curves 1 in Figures 6 and 7). The comparison of curve 2 in Figure 6 and curve 4 in Figure 7 clearly shows that the stability of the electrets, made of PTFE films modified with tetraethoxysilane, is appreciably enhanced after the thermal treatment. However, the thermal treatment of the films modified with tetrabutyl titanate and orthophosphoric acid (Figure 7, curves 2 and 3) results in decrease of the thermal stability of charge. The shape of the curves suggests that the surface potential decay is influenced by the following factors. First, the fraction of charge trapped in the new deep surface traps is diminished. Second, probably as a result of desorption, the low temperature relaxation, inherent to non-modified films, can be observed.

4 CONCLUSION

Chemically modified LDPE and PTFE films containing various nanosized groups on the surface were produced and their electret properties were investigated. The main results of the investigation can be summarized as follows:

- When LDPE films are treated with phosphorus trichloride vapors, the phosphorus-containing groups are attached to the reactive sites on the polymer surface.
- The gas-phase modification considerably increases the magnitude and stability of the electret charge in LDPE films. The increase in the magnitude of the stable homocharge is made possible by the fact that the “crossover” phenomenon is not observed in the modified LDPE films. This has been achieved by means of charge trapping in the new traps that belong to the phosphorus-containing nanosized groups formed on the polymer surface. Besides, these groups decrease the molecular mobility on the surface of LDPE. This, in turn, leads to the decrease of the probability of charge activation from the surface traps.
- The phenomenon of positive charge stabilization was found in PTFE films with the surface chemically modified by means of wet treatment with three different reagents: orthophosphoric acid, tetrabutyl titanate, and tetraethoxysilane. These reagents interact with the surface

defects in PTFE, forming functional groups, capable of efficient capturing and storing of the positive homocharge.

- The result of combined treatment of PTFE films, which includes surface modification with subsequent thermal treatment at 305-310 °C, is dependent on the chemicals used for the surface modification. The films modified with orthophosphoric acid and tetrabutyl titanate, after the thermal treatment, display the low-temperature relaxation process, inherent to non-modified films. Also, the fraction of the stable homocharge is diminished. Conversely, PTFE films modified with tetraethoxysilane display even higher charge stability after the thermal treatment.

Thus, by chemically modifying the surface, we have considerably enhanced the electret state stability in LDPE and PTFE films. Hence such polymers with chemically modified surface appear to be very promising electret materials for device applications.

ACKNOWLEDGMENTS

The authors would like to thank Dr. Sergey Trifonov of St. Petersburg State Institute of Technology (St. Petersburg, Russia) for the samples of LDPE films modified with phosphorus trichloride vapors. Also the authors wish to extend their thanks to Dr. Andreas Holländer of Fraunhofer Institute for Applied Polymer Research (Potsdam, Germany) for the help with XPS measurements.

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