

PP film electrets obtained at different temperatures and irradiated by a low energy laser

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The paper studies the influence of low-energy laser radiation on the electret performance of polypropylene (PP) corona electrets. A 20 μm PP foil was charged in a positive and negative corona at 20 °C and 80 °C. The corona voltage was $\pm 5\text{kV}$, while that of the grid was $\pm 1\text{kV}$. The surface potential was measured using the method of the vibrating electrode with compensation. The electrets obtained were subjected to low-energy CO_2 laser radiation with different exposure times, until a steady level was achieved. The drop in the relative surface potential versus irradiation energy was studied, and an exponential dependence was found.

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1. Introduction

The study of the interaction of low energy laser radiation with polymer electret films is motivated not only by scientific but also by applied research interests.

A system for information storage and retrieval on dielectric materials using the selective formation of electret locations by modulated laser beams has been considered [1]. A reading system establishes the presence or absence of an electric field created by the stored charge on the electret locations in the dielectric tape. In [2], electrets with a suitable charge density and long lifetime for the fabrication of electret floppy disks for digital storage of information have been studied. To store electret charges for a long time, the dielectric materials should have constant and stable properties over a large temperature and frequency range. Polyolefin polymers, among which polypropylene is the most widely used, have been found [3] to be very suitable materials for this purpose. This is due to their low cost, low density, high thermal stability, resistance to corrosion, low relative weight. It has been shown in [4] that CO_2 laser radiation allows direct laser writing of mid-infrared microelements on polyethylene. The bonding of non-polar polymer films (PE, PP) to various polymer substrates is a problem, and needs costly preliminary treatment. In [5], an alternative tunable CO_2 laser processing of the polypropylene substrate is suggested, which improves its adhesive properties. A PE-PP-PE film sandwich structure is obtained in this way. It has been found that the resonance absorption of IR light causes changes in the chemical structure of PP, similar to those in polyethylene and polysulfone, but under exposure to much lower energy densities. The effect is of importance for the direct storage of information in polymer films, as well as in the laser

welding of PP. In [6], it has been shown that the relative surface potential of positive and negative polypropylene corona electrets does not change upon irradiation with low energy He-Ne and CuBr vapour laser radiation. These, as well as visible semiconductor lasers, could therefore be used for the multiple reading of information stored by an electrostatic field on polymer electrets.

The aim of the present paper is to investigate the influence of low energy CO_2 laser radiation on PP electrets obtained at different temperatures (20 °C and 80 °C).

2. Experimental details

Electret samples prepared from a 20 μm isotactic polypropylene film, supplied by Assenova Krepost Ltd., have been studied. The films were initially cleaned in alcohol in an ultrasonic bath for 4 minutes (2 minutes for each side), washed in distilled water and dried on filter paper.

Circularly shaped samples were cut out and placed in a holder, ensuring the same surface during charging, irradiation and measurement, which coincided with the laser beam cross-section.

Samples of polypropylene were charged in a point-to-plane corona discharge at $\pm 5\text{ kV}$ with an air gap of 4 cm and a grid voltage $V_g = \pm 1\text{ kV}$. The charging of the samples was performed for 1 minute at two different temperatures (T_{ch}) 20 °C and 80 °C

The surface potential of the electrets was measured using the method of the vibrating electrode with compensation, the error not exceeding 5%. The initial surface potential V_0 of the obtained electrets was measured. Then they were irradiated with a quasi-continuous wave CO_2 laser (10,6 μm), at an average power

of 4 W. The laser beam cross-section crossing the sample coincided with the free surface, having a circular shape 8 mm in diameter. The samples were irradiated over different time intervals, so that a range of 2000J for the cumulative energy was covered. After the irradiation, the surface potential V_{irr} was measured again, and the relative surface potential V_{irr}/V_0 was calculated, and each result was averaged over five measurements. Finally, V_{irr}/V_0 was plotted versus the cumulative energy E .

For some of the samples, XPS measurements were taken in a high vacuum chamber of an Escalab MK II electronic spectrometer (VG Scientific) at a pressure of $1 \cdot 10^{-8}$ Pa. The photoelectronic spectra were generated by a AlK_{α} anode ($h\nu = 1486,6$ eV) and a resolution of 0.1 eV. The spectra of the C1s, O1s and N1s lines were recorded. All recorded lines were calibrated to the C1s line at 284.6eV. The surface concentrations were obtained as the ratio of the peak intensities and the photoionization cross-section.

3. Results

Fig. 1 and Fig. 2 show the experimental dependences of the relative surface potential on the cumulative energy, for laser irradiated positively and negatively charged electrets. The plots were obtained for two different charging temperatures (T_{ch}): 20 °C and 80 °C. The error bars show the 90% confidence intervals for the average values of the relative potential.

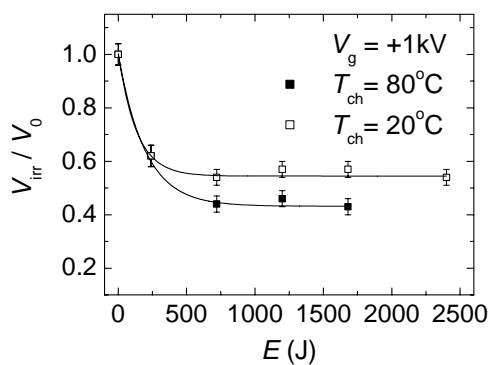


Fig. 1. Dependence of the relative surface potential of positive PP electret samples on the energy of CO_2 laser radiation.

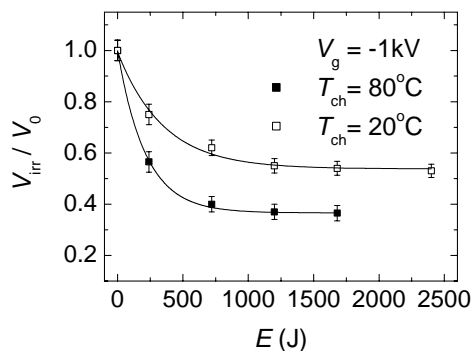


Fig. 2. Dependence of the relative surface potential of negative PP electret samples on the energy of CO_2 laser radiation.

The experimental results in Fig. 1 and Fig. 2 show that the relative surface potential V_{irr}/V_0 drops with the cumulative irradiation energy, following an exponential curve independently of the polarity and temperature of the charging. For samples charged in a positive corona, the decrease with the energy is faster and for a cumulative energy of approximately 750 J, V_{irr}/V_0 reaches a steady state level which does not change with the further increases in the energy. For electrets charged at 20 °C, $(V_{\text{irr}}/V_0)_{\text{st}} = 0.54$ while for those at 80 °C - $(V_{\text{irr}}/V_0)_{\text{st}} = 0.43$. For electrets charged in a negative corona, the steady state $(V_{\text{irr}}/V_0)_{\text{st}}$ is reached at greater cumulative energies of about 1000 J, and for samples charged at 20 °C it is $(V_{\text{irr}}/V_0)_{\text{st}} = 0.54$ while for those at 80 °C $(V_{\text{irr}}/V_0)_{\text{st}} = 0.37$ (Fig. 2). Therefore, lower values for $(V_{\text{irr}}/V_0)_{\text{st}}$ have been found for the samples charged at a higher temperature (80°C), compared to those for the electrets charged at 20°C, independently of the corona polarity.

The spectra of the C1s, O1s and N1s lines for the samples charged at $V_g = \pm 1$ kV and $T_{\text{ch}} = 20$ °C and 80 °C and irradiated with a CO_2 laser with a cumulative energy of 1000 J, were recorded. This is the energy at which all samples reach a steady state. No presence of nitrogen was identified for any of the samples. Table 1 shows the results for the C1s and O1s peaks and the O/C atomic ratio for the samples.

Table 1. XPS data for PP corona electrets.

SAMPLES			Irradiated		
No	V_g (kV)	T_{ch} (°C)	C (at%)	O (at%)	O/C at. ratio
1	+1	20	99.32	0.68	0.0068
2	-1	20	98.75	1.25	0.0126
3	+1	80	98.99	1.01	0.0102
4	-1	80	99.10	0.90	0.0090

4. Discussion

We assume that during the charging of the polypropylene samples, an adsorption of charged particles takes place. As shown in [7,8] for charging parameters like ours, a stable surface and not a volume charge is formed. We therefore cannot assume any absorption process.

The corona discharge creates high energy charged oxygen-containing particles like ions and ion groups [9]. These particles are accelerated by the electric field of the corona and interact with the surface of the PP. Depending on the type of interaction, we have physical or chemical adsorption of charged particles, which determines the surface potential of the resulting electret. It is hard to determine which part of the electret charge is due to chemical adsorption characterized by a much. For this purpose, we measured the relative surface potential (V/V_0) of samples charged at $V_g = \pm 1$ kV and $T_{\text{ch}} = 20$ °C and kept in a vacuum chamber at 20 °C at different pressures

$p = (10^{-2} \text{ to } 10^{-4})$ torr for 30 min. For $p = 10^{-2}$ torr in the case of positively charged samples, we obtained $V/V_0 = 0.3$ and for negatively charged samples $V/V_0 = 0.2$. These values did not change on decreasing the pressure, and should therefore determine the part of the adsorbed particles with higher bonding energy. Analogous results have been reported [10] for Trycite and Mylar. For $p \leq 10$ torr, $V/V_0 \approx 0.3$ and remains constant when the pressure is reduced at room temperature.

Upon laser irradiation of the PP electret samples, the opposite process - desorption - can occur on the surface, as a result of energy interactions. Since this is stimulated by the laser radiation, it is called laser desorption [11]. It has been shown [5] that when thin PP films are irradiated with a CO₂ laser, a resonance absorption of coherent light takes place and a strong thermal effect is observed, rather than an optical one. In this case, we can talk about laser thermodesorption of the charged particles from the electret surface, which causes the reduction in its surface potential. This assumption is confirmed by the experimentally obtained dependencies of the relative surface potential on the irradiation energy (Fig. 1 and Fig. 2).

For all groups of samples under study (Table 1), the experimental results fitted very well to an exponential dependence of the type:

$$y = y_{\infty} + (1 - y_{\infty}) \exp\left(-\frac{E}{E_{\infty}}\right) \quad (1)$$

where $y = V_{\text{irr}}/V_0$ is the relative surface potential, $y_{\infty} = (V_{\text{irr}}/V_0)_{\text{st}}$ is the steady state level which is reached for $E \gg E_{\infty}$ and E_{∞} is a constant characterising the process.

Eq. (1) is analogous to an equation characterizing the kinetics of adsorption-desorption processes [11]. In our case, these processes are not parallel but in series. Firstly, during the corona discharge, an adsorption takes place, as a result of which the accumulated surface charge determines V_0 at $E = 0$. Subsequently, laser thermodesorption, depending on the irradiation energy, takes place upon CO₂ laser irradiation, and its development is described by the second term in eq. (1). Above a certain value of the energy ($E \gg E_{\infty}$), the quantity of desorbed particles remains the same. At that point, the steady state level of the relative potential y_{∞} can be determined.

XPS studies have been carried out for all groups of samples in this state (Table 1).

In Table 2, we compared the O/C atomic ratio for irradiated and non-irradiated samples.

For all irradiated samples, we observe a decrease of the O/C atomic ratio, which shows a decrease of the quantity of oxygen. As all charged groups of particles creating the electric charge are oxygen-containing [9], this implies a reduction of the relative surface potential V_{irr}/V_0 , as observed experimentally.

Table 2. O/C atomic ratios for PP corona electrets.

No	SAMPLES		$\frac{(O/C)_{\text{irr}}}{(O/C)_{\text{non}}}$
	Irradiated	Non-Irradiated.	
	(O/C)irr at. ratio	(O/C)non at. ratio	
1	0,0068	0,0200	0,34
2	0,0126	0,0369	0,34
3	0,0102	0,0120	0,85
4	0,0090	0,0290	0,31

For the samples charged at 20 °C, the relative change in the O/C atomic ratio is identical (0.34), as is that of $y_{\infty} = (V_{\text{irr}}/V_0)_{\text{st}} = 0.54$. The higher relative reduction in the oxygen contents with respect to the electret charge could be explained with the assumption of the presence of a thermo-desorption of non-charged oxygen-containing particles. It is known that there exists a certain quantity of oxygen on the surface of non-charged PP films, which depends on the concentration of surface impurities [12].

For the samples charged at 80 °C, the corona polarity influences the relative changes of the O/C from 1 when $E_{\text{irr}} = 0$ to the different values of the $(O/C)_{\text{irr}}/(O/C)_{\text{non}}$. For those charged in a negative corona it is 0.31, and the decreasing is a little greater than those of $V_{\text{irr}}/V_0 = 0.37$. We can assume a weaker thermo-desorption of neutral oxygen. For the samples charged in a positive corona, however, we observed a much weaker decreasing in the relative O/C atomic ratio (0.85) compared to the decreasing of $V_{\text{irr}}/V_0 = 0.43$. This may be due to thermal oxidation during CO₂ laser irradiation, which is made easier by the modification of the surface upon charging at a higher temperature.

4. Conclusions

The influence of low energy CO₂ laser irradiation on PP electret films, obtained in positive and negative coronas at two different temperatures (20 °C and 80 °C) was investigated. For all samples, the decrease in the relative surface potential with the cumulated energy followed an exponential dependence, and a steady state level $(V_{\text{irr}}/V_0)_{\text{st}}$ was eventually reached. For the samples charged at 80 °C, $(V_{\text{irr}}/V_0)_{\text{st}}$ was lower than for those charged at 20 °C. The observed behaviour is explained by the consecutive occurrence of two processes: adsorption of oxygen containing ions or ion groups during the corona discharge, and laser thermo-desorption during CO₂ laser irradiation, which depends on the cumulative energy of the laser radiation.

The different steady state $(V_{\text{irr}}/V_0)_{\text{st}}$ values for PP electrets obtained under different conditions after being irradiated with a CO₂ laser can find applications in optical storage and the processing of information on PP films, as for example the direct registration of information on thin PP electret films using a low energy CO₂ laser.

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