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Corona-charged polypropylene films investigated by a laser refractometer

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Optical and electret characteristics of thin 20 µm polypropylene (PP) corona electrets have been studied in the present work. Refractive index (RI) in a surface layer with submicrometer thickness was determined by the method of the disappearing diffraction pattern. Electret surface potential was measured by the method of the vibrating electrode with compensation. The analysis showed that electret charge was mainly deposited onto the charged surfaces. The measured RI values for the electret samples were higher than those for the uncharged samples. We assumed it was due to surface structural changes in the PP films that occurred during corona charging.

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1. Introduction

During the last years polymer electrets have extensively been studied because of their good properties to store electret charge and be made in the form of thin films [1-3]. The interest in those studies is a consequence of the largely enhanced usage of electret thin films in various applications. One of the methods that is often used to produce electrets from polymer films is the corona discharge method. Polypropylene (PP) is widely used in practice to obtain corona electrets [4-5]. Hence, electret behaviour of thin PP films is quite intensively investigated making use of different methods [6]. There are no references, however, to studies that relate the electret properties of PP films to their optical properties, and in particular to refraction index and absorption. Such studies have only been carried out with uncharged PP films in connection to exploring their structure and film thickness [7-9].

A refractive index (RI) measurement with conventional Abbe and Pulfrich refractometers is not possible, because thickness is less than 30µm that makes it impossible to exactly determine critical angle. Recently, a new method has been proposed for RI measurements of very small samples or microliter droplets – the method of the disappearing diffraction pattern (MDDP) [10].

Thin PP positive and negative corona electrets have been studied in the present work by the method of the disappearing diffraction pattern. It have been used a two-wavelength laser refractometer (TWLR) to determine refractive index (RI) in a surface layer with a submicrometer thickness.

2. Experiment

We have studied samples of isotactic polypropylene (PP) film, 20 µm thick, manufactured by Assenova Krepost Ltd, Bulgaria. Film was initially cleaned in alcohol in an ultrasonic bath for 4 minutes, washed in distilled water, and dried on filter paper. From the clean film we cut rectangular samples: $(3 \times 2)\text{cm}^2$.

Electrets were obtained by the corona discharge method. For that purpose samples were charged for 1 minute by a three-electrode system consisting of a corona electrode (needle), a grounded plate electrode, and a metal grid placed between them. Samples were placed on the grounded plate electrode. Positive or negative 5kV voltage was supplied to the corona electrode. Grid voltage had the polarity of the corona electrode, the voltage was set to U_g=350V, 500V, 650V, 800V, and 950V respectively. Electrets were charged under room conditions. After charging the initial surface potential U_0 was measured.

Electret surface potential was measured by the method of the vibrating electrode with compensation; by which the estimated error was better than 5% for voltages greater than 100 V.

For all electret samples refractive index was measured by the method of the disappearing diffraction pattern (MDDP) using a two-wavelength laser refractometer (TWLR). Fig. 1 represents the schematic drawing of a TWLR.

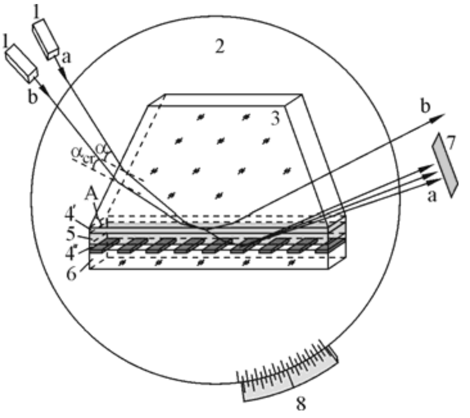

Fig. 1. Experimental set-up: (1) laser; (2) rotary stage with 1 arcmin resolution; (3) glass prism with RI =N; (4′), (4″) liquid layer,(5) sample; (6) reflecting grating; (7) screen; (8) vernier.

Two lasers were used as light sources (1): He-Ne "Spectra Physics" (0.5 mW), and Laser pointer (0.1 mW) generating at 632.8nm and 532 nm respectively. A sample (5) was put between the glass prism (3) and the reflecting grating (6). To ensure a good optical contact at both sides of the sample a thin layer of contact liquid having an appropriate refractive index was coated – benzyl alcohol – n_r(632.8 nm)=1.5374, n_g(532 nm)=1.5449.

The angle of the incident laser beam on the prism's side wall was denoted as α. That angle α changed whenever the rotary stage (2), where the prism with the sample and the reflecting grating were firmly fixed, rotated. At a certain incidence angle α, the laser beam refracted consecutively by the prism (3), the liquid layer (4′), the sample (5), the liquid layer (4″), and reached the reflecting grating (6). A diffraction pattern was observed on the screen (7) (beam path (a) as shown in Fig.1). If the angle α was reduced to a certain critical value α_{cr} a total internal reflection (TIR) occur at the liquid (4′) – sample (5) interface. Hence, the laser beam did not reach the reflecting grating and a diffraction pattern was not observed on the screen (beam path (b) as shown in Fig.1). We fixed the position of the rotary stage at which the diffraction pattern disappeared from the screen. Then we used the graduated circle with a vernier (8) to measure the critical angle α_{cr}, with an accuracy of 1′.

Knowing α_{cr} we could calculate sample RI by the following relation:

$$n = N \sin\left[A \pm \arcsin\frac{\sin\alpha_{cr}}{N}\right] \qquad (1)$$

where A was prism refractive angle, and N – prism refractive index. In our experiment A = 65°, N(532 nm)=1.7480, N(632.8 nm)=1.7347.

The sign (+) and (-) correspond to clockwise and counter-clockwise determination of α_{cr}, respectively.

We carried out an additional experiment in order to determine the contact liquid influence on electret sample charge. All samples were divided into three groups, each one comprising 6 samples which were charged at different grid voltages: ±350V; ±600V; ±850V respectively. After charging the initial surface potential U_0 was measured. Then each sample was placed for 1 minute between two glass slides coated by a thin benzyl alcohol layer at their both sides. That was the minimal period of time for which the experimental set-up was tuned and the samples were dipped in benzyl alcohol before their RI was measured. The samples were then taken out, dried on filter paper, and their surface potential U_1 was measured again. The relative surface potential U_1/U_0 was calculated.

3. Results

All electret samples were divided into 10 groups according to their charging conditions (corona polarity, grid voltage) (Table 1). A group of reference samples – samples that were not corona charged – was measured too. We studied 6 samples from each of the groups. Initial surface potential U_0 and critical angle α_{cr} were measured for each one of the samples, and α_{cr} values were used to calculate RI by the formula (1). Table 1 represents the experimental data. The dependence of RI on the initial surface potential U_0 for the wavelength of 532 nm is plotted in Fig. 2, and for the wavelength of 632.8 nm – in Fig. 3. Dots denote the average values for RI, and error bars – the confidence intervals, at 90% confidence level. The maximum standard deviation from the average value for RI at 90% confidence level was 5×10^{-4}.

Table 1. The experimental data for the refractive index and the initial surface potential.

$\lvert U_g \rvert$ V	Group	U_0 (V)	n_g /532nm/	n_r /632.8nm/
0	Ref.	0	1.5078	1.5056
350	1.1	-259	1.5157	1.5120
500	1.2	-371	1.5159	1.5123
650	1.3	-488	1.5152	1.5117
800	1.4	-593	1.5152	1.5117
1000	1.5	-737	1.5157	1.5120
350	2.1	+270	1.5159	1.5126
500	2.2	+340	1.5152	1.5121
650	2.3	+476	1.5159	1.5126
800	2.4	+542	1.5149	1.5118
1000	2.5	+733	1.5155	1.5123

The results we obtained showed that the RI values for the uncharged samples (1.5078 for λ=532 nm, and 1.5056 for λ=632.8 nm) were lower than those for the electret samples. The electret samples RI did not depend on corona polarity and surface potential values. The electret sample average RI value was 1.5154 for λ=532 nm and 1.5122 for λ=632.8 nm.

Table 2 represents the results for how surface potential changed at coating electret samples with benzyl alcohol.

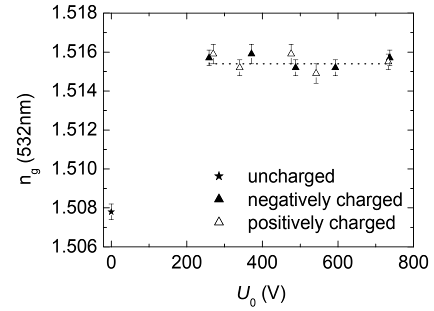

Fig. 2. The dependence of RI on the initial surface potential U_0 for λ=532 nm.

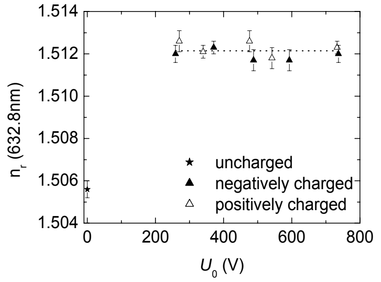

Fig. 3. The dependence of RI on the initial surface potential U_0 for λ=632.8 nm.

Table 2. Surface potential of coating electret samples with benzyl alcohol.

IU_gI (V)	Group	U_0 (V)	U_1 (V)	U_1/U_0
350	1-1	-309	8	0.026
600	1-2	-514	9	0.018
850	1-3	-712	10	0.014
350	2-1	+311	14	0.045
600	2-2	+508	15	0.029
850	2-3	+654	16	0.024

It was evident that if electret samples were coated by benzyl alcohol, surface potential changed substantially after 1 minute to a certain value that did not depend on initial surface potential and only on corona polarity. For the positively charged electrets U_1 = (15 ± 1) V, and for the negatively charged U_1 = (9 ± 1) V. As the measured values for U_1 were very small, the measurement inaccuracy was greater and was in the order of 10%. For the positively charged samples relative surface potential U_1/U_0 had a larger value compared to the one for the negatively charged samples. Moreover, when U_0 increased, U_1/U_0 decreased.

4. Discussion

Material refractive index is connected to material polarizability and in its turn it depends on the availability of free and bound charges. When samples are corona charged at various grid voltages different quantities of electrical charges are injected into the samples, so the values of the measured initial surface potential U_0 are different (Table 1). Therefore, we should expect different RI values for the different electret groups. Experimental results, however, showed that for all measured electret samples RI was the same.

In order to clarify this contradiction we made the following assumptions:

A) In the case of PP corona electrets almost the whole amount of the electric charge is deposited on sample surfaces, and only a small part of the charge is injected into a certain depth of the bulk. Such charge distribution was reported for negatively charged 50μm PP corona electrets using the LIPP and TSC methods [11].

B) When samples are coated by benzyl alcohol for 1 minute, their surface charge is removed. Furthermore, the charge that is injected into the volume does not change as benzyl alcohol cannot penetrate into the samples. The fast surface potential discharge is caused by the great difference in volume resistivity values for PP films (~10^{17} Ohm.m) and benzyl alcohol (~10^7 Ohm.m). That assumption agrees well with [11] where it was found that negatively charged 50 μm PP films got their surface charge removed for just 1 second when dipped in ethanol.

If surface potential is measured by the vibrating electrode method, one registers both surface charge and volume charge: $U = f(\sigma_{\text{eff}})$. The effective surface density of the charge σ_{eff} is a basic characteristic for the electrets and it depends on the actual component correlation – polarization P and injected charges with surface density σ – at the surface and in the bulk, where $\sigma_{\text{eff}} = \sigma - P$.

Hence, considering the assumptions we have made, the measured surface potential for electrets that have previously been coated by benzyl alcohol is only due to the injected charge trapped in electret bulk. And that is the reason for the very low U_1 values (Table 2). In order to give an account of the influence of those volume charges in the measurements of refractive index by the MDDP method we calculated laser irradiation penetration depth into the sample.

The thickness of the layer where RI is measured depends on light energy penetration into the sample during the TIR. In order to obtain quantitative estimation of the energy flow penetration depth d_0, we should emphasize that our consideration is restricted near the critical angle $\alpha \in [\alpha_{\text{cr}}, \alpha_{\text{cr}} + \delta]$, where δ is connected with the rotary stage's resolution, and in practice δ <<1. A good approximation for this case is

$$\sin\alpha \approx \sin(\alpha_{\text{cr}} + \delta) \approx \sin\alpha_{\text{cr}} + \delta.\cos\alpha_{\text{cr}} \qquad (2)$$

where $\sin\alpha_{\text{cr}} = n_{\text{sample}}/N = n_{21}$.

The energy flow penetration depth d_0 is caused by the Goos-Hänchen (G-H) shift [7] and from geometrical consideration

$$d_0 = d/2\sin\alpha \qquad (3)$$

where d is G-H longitudinal shift, strongly depending on the state of polarization. According to the Renard's treatment [8] for TE (s) and TM (p) polarizations, near the α_{cr} we have

$$\begin{aligned} d_{\mathrm{s}} &= \frac{\lambda_0}{2\pi n_1\left[\sin^2(\alpha_{\mathrm{cr}}+\delta)-n_{21}^2\right]^{1/2}} = \\ &= \frac{\lambda_0}{2^{3/2}\pi n_1\sqrt{n_{21}}\left(1-n_{21}^2\right)^{1/4}\sqrt{\delta}} \\ d_{\mathrm{p}} &= n_{21}^{-2}.d_{\mathrm{s}}, \end{aligned} \tag{4}$$

where λ_0 is vacuum wavelength.

It should be mentioned, that the obtained value d_{s} coincides with the evanescent wave's characteristic length, describing exponential decay of the wave into a second, optically less dense medium during TIR. That length does not depend on wave's polarization. This fact is well known, but still in many optical books the authors use "penetration depth" improperly.

From (3) and (4) we have the following relation for circularly polarized wave:

$$\begin{aligned} d_0 &= \frac{\lambda_0.\left(1+n_{21}^4\right)^{1/2}}{\pi n_1\left(2n_{21}\right)^{5/2}.\left(1-n_{21}^2\right)^{1/4}}.(2\delta)^{-1/2} = \\ &= \frac{0.0589.10^{-2}}{\sqrt{\delta}} \end{aligned} \tag{5}$$

Let us estimate d_0 for our experimental condition: $\lambda_0 = 0.633\,\mu\mathrm{m}$; $n_1 = 1.735$; $n_{21} \cong 0.875$ and $\delta =$ 5arcmin; from (5) we have $d_0 = 0.98\,\mu\mathrm{m}$, so our RI values are determined in the near surface layer with thickness $\approx 1.5\lambda_0$. For $\lambda_0 = 0.532\,\mu\mathrm{m}$ we estimated less value $d_0 = 0.82\,\mu\mathrm{m}$.

For the laser irradiation ($\lambda_0 = 0.633\,\mu\mathrm{m}$) penetration depth into the sample we calculated $d_0 = 0.98\,\mu\mathrm{m}$. It was found out in [11] that volume injected charge was at 7 µm from the negatively charged surface of a 50 µm PP corona electret. It was shown in [6] that penetration depth for charges injected into the volume of various electrets was proportional to corona voltage (charging field). As in our case corona voltage is 6 times less than that in [11], injected charges should penetrate into the volume at a depth that is 6 times smaller, i.e. ~ 1.2 µm, that is more than $d_0 = 0.98\,\mu\mathrm{m}$.

The calculations we have made show that the laser irradiation penetration depth d_0 was smaller than the depth of the volume injected charges. Therefore, when RI was measured the influence of the volume injected charge was not taken into account. Electret surface charge did not influence RI measurements too, as it was removed by benzyl alcohol coating. Nevertheless, RI for the electret samples was higher than RI for the reference uncharged samples and did not depend on surface potential value and polarity. Most probably that was due to structural changes of electret surfaces that occurred at the time of corona charging and did not depend on U_{g}. Those could be broken or newly formed bonds, generated specific surface defects, additionally captured oxygen containing groups etc. [14]

5. Conclusion

For the first time in the present paper 20 µm thin polypropylene (PP) corona electrets (positively and negatively charged) were studied by the method of disappearing diffraction pattern (MDDP) used to determine refractive index (RI) of a surface layer with a submicrometer thickness d_0.

The analysis of the measured optical (refractive index) and electret (surface potential) characteristics of thin PP films showed that electret charge was mainly deposited onto the charged surfaces for both positive and negative corona electrets. Only a small portion of the charge (1.4% - 4.5%) was injected into the volume at a depth that was greater than the laser irradiation penetration depth d_0. The value of d_0 was calculated to be 0.98 µm for $\lambda_0 = 0.633\,\mu\mathrm{m}$ and 0.82 µm for $\lambda_0 = 0.532\,\mu\mathrm{m}$

The measured RI values for all the studied groups of electret samples were the same and were higher than those for the reference uncharged samples. We assumed that this was due to surface structural changes in the PP films that occurred during corona charging.

Hence, the MDDP method used to measure RI in thin transparent polymer films can be used to determine their former history, i.e. to find out if surface modifications have occurred at a submicrometer depth ~ d_0, caused by ageing or various influences – charging in electric field, heating, mechanical deformation, irradiation by various beams, etc.

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