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# Refractometric investigations of thin organic films

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We have investigated the refractive indices (RI) of different polymer and gelatine films using a specially constructed two-wavelength laser refractometer. The critical angle is determined by the disappearance of the diffraction orders, well separated by the metal grating at 532 and 632.8 nm. The following polymers have been investigated: “Styrenic-A”, “Polyacrylate”, “Paraloid B72” and “Cellulose” as well as normal and $Cr^{3+}$-hardened gelatine. The data obtained from the two-wavelength RI measurements are used for the dispersiometric analysis following Wemple and DiDomenico’s one-oscillatory model. RI differences between the sample-air and the sample-substrate interfaces are identified. In the case of normal gelatine, this difference depends on the type of substrate. Based on the Lorentz- Lorenz relation, the RI change is attributed to the density increase, governed by the adhesion forces, as well as the free volume re-distribution near the sample surface. The polar and dispersion components of the free surface energy of the substrate and gelatine layer are determined. On the basis of the results, the reversible work of the adhesion between the gelatine layer and different substrates is estimated.

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## 1. Introduction

Optical polymers (OP), with their excellent transparency, low price, simple technology and good mechanical properties are very attractive for many optical applications. An extremely good introduction to polymer optics is, for example, Meeten’s monograph [1]. Nowadays, however, lasers gradually replace the classical light sources, so investigations at laser wavelengths rapidly increase. Recently, the refractive index (RI) and dispersion characteristics of 16 optical polymers had been obtained [2, 3]. As in a previous investigation [4], the sample thickness was varyied from 2.5 to 5.5mm. In many applications, however, the optical elements are much thinner, ~ 20μm, and it is important to obtain RI and dispersion information for thin OP films in the visible spectral range. It has been earlier established that RI of PMMA exponentially decreases with diminishing sample thickness, and in the 10-0.25μm thickness range the RI difference is 0.0147 [5].

The purpose of the present paper is to study the RI of optical polymers at two wavelengths and to calculate their dispersion coefficient. The influence of surface energy of the substrate on the RI changes of polymers is also studied.

## 2. Experimental

### 2.1. Sample preparation

The optical polymers-cellulose, Styrenic A, Paraloid B72, and Polyacrylate were dissolved in suitable solvents. Different concentrations were used to obtain film thicknesses varying from 4 to 28 μm, coated on glass substrates. The samples were dried at 20°C. The first two samples before measurements were separated from the substrates.

Water gelatine (Rousselot) solutions were coated on different substrates - glass, PMMA, Polyacetate, and Polyester. The hardened gelatine films were prepared with $Cr^{3+}$ ions. After drying at 20°C, the films were also separated from the substrate.

### 2.2. Instrumental

For the RI measurements and dispersion characterization, a two-wavelength laser refractometer was constructed. The main objectives were: 1.- to minimize the mechanical imperfections; 2.- to avoid temperature control during the measurements. The device is schematically shown in Fig. 1.

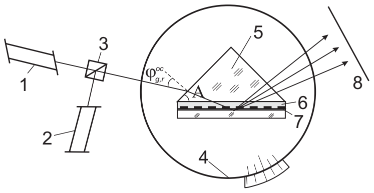

*Fig. 1. Principle scheme of laser refractometer: 1 – He-Ne laser; 2-Laser pointer; 3-beam splitter; 4-goniometer; 5 - heavy flint - glass prism; 6 - sample; 7- metal grating; 8-screen.*

As laser sources He-Ne "Spectra-Physics" 0.5mW and 0.1 mW pointers were used, generating at 632.8 and 532 nm, respectively. In brief, the principle of the critical angle determination is as follows: when the incidence angle $\varphi^{o}_{g,r}$ for both wavelengths is above the corresponding critical angles $\varphi^{oc}_{g,r}$, both laser beams pass through the sample (6) and on the screen (8) red and green diffraction orders are observed. As a result of the goniometric Table 6 rotation, first the green, and then the red diffraction patterns disappear, thus indicating the values of the corresponding critical angles. During the measurement time- 0.5 – 1.0s, the temperature is unchanged and mechanical imperfections are avoided. The corresponding RI was calculated by the following relation:

$$n_{g,r} = N_{g,r} \sin\left[ A \pm \sin^{-1}\left( \frac{\sin\varphi^{oc}_{g,r}}{N_{g,r}} \right) \right], \qquad (1)$$

where the symbols "g" and "r" are for the 532 and 632.8 nm wavelengths, respectively; $A$ is the prism (5) refracting angle, in our case – 65 deg.

The prism wasis made from heavy flint-glass TF-4, Russian production, with RI's $N_g$ = 1.748 and $N_r$ = 1.735.

The experimental uncertainty mainly depends on the angular resolution Δφ of the goniometric table - Microcontrole TR 80 : $\Delta\varphi^{o}$ = 1arcmin ~ 3.10$^{-4}$. After differentiation of the relation (1), it is easily to show that for small critical angles in air (as in the present work), we have as a good approximation:

$$\Delta n_{g,r} \approx \cos A.\Delta\varphi \;\; \leq \cos 60^{o}.\Delta\varphi = 2.10^{-4} \qquad (2)$$

The refractive indexes of gelatines, cellulose $n_a$ and Styrenic A films were measured after separation from the glass substrates. The RI value of the air-film interface ($n_a$) and the film-substrate interface ($n_s$) were obtained using a matching liquid – methylene iodide ($CH_2I_2$). The film thickness was measured with a Mitutoyo digital micrometer (experimental error ± 1μm).

## 3. Results and discussion

In Table 1, the obtained RI values of gelatines, cellulose $n_a$ and Styrenic A films at different film thicknesses and wavelengths are given. First of all, it should be noted, that near the substrate an increase in RI is observed for all measured samples. The largest RI difference ($n_s - n_a$) was observed for Styrenic A – 0.019, and the smallest one for gelatines.

*Table 1. Refractive index dependence on position, thickness and wavelength.*

| Sample | *d*, μm | Wavelength | | | |
|---|---|---|---|---|---|
| | | 532 nm | | 632.8 nm | |
| | | $n_a$ | $n_s$ | $n_a$ | $n_s$ |
| Gelatine, non-hardened | 18 | 1.551 | 1.553 | 1.534 | 1.535 |
| Gelatine, hardened | 14 | 1.544 | 1.545 | 1.533 | 1.535 |
| Cellulose | 17 | 1.476 | 1.479 | 1.475 | 1.483 |
| | 11 | 1.480 | 1.488 | 1.472 | 1.477 |
| Styrenic A | 18 | 1.506 | 1.523 | 1.504 | 1.521 |
| | 10 | 1.505 | 1.524 | 1.503 | 1.518 |

It is interesting to compare our thin film results with those obtained in [3], where the sample thickness was between 2.5 and 5.1 mm. Very good agreement is observed for $n_s$ of Styrenic A, $d$ = 10 μm, where the RI difference is only 0.001. For the other optical plastics- Polyacrylate and Cellulose, the differences (for $n_a$) are ≤ 0.005.

The Paraloid B72 and Polyacrylate have very strong adhesion and have not been removed undamaged. Their air-films RI strongly increased with the thickness diminishing in the 28 - 4μm range. This behaviour is illustrated in Fig. 2 for 532 and 632.8 nm wavelengths.

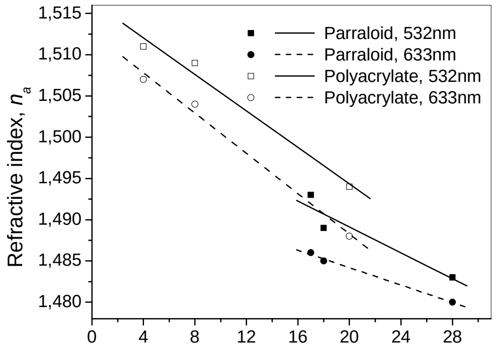

*Fig. 2. The air-film RI dependence.*

As seen, the RI of the hardened gelatine is lower than that of the non-hardened one. In the green spectral range, this difference is higher. A possible reason could be the competition between the density, molecular weight and polarization contributions to the RI. In order to elucidate this, we have used the Lorentz-Lorenz relationship (see [1], p. 46):

$$\frac{n^2-1}{n^2+2}\cdot\frac{M}{\rho}=\frac{10^3 N_A}{3\varepsilon_o}\alpha \qquad (3)$$

where: $M$ is the molecular weight, $\rho$ the density, $\alpha$ the polarization, $N_A$ is Avogadro constant and $\varepsilon_0$ is the free space permittivity.

By differentiating (3) we have:

$$\left(\frac{\Delta n}{n}\right)=\frac{(n^2-1)(n^2+2)}{6n^2}\left[\left(\frac{\Delta\alpha}{\alpha}\right)+\left(\frac{\Delta\rho}{\rho}\right)-\left(\frac{\Delta M}{M}\right)\right] \qquad (4)$$

The hardening process is connected with a strong increase in the inter-molecular cross-linking by $Cr^{3+}$ ions that makes the last term in the square brackets dominate. The highly hardened membrane at the surface [6] is the main reason for the low RI and the observed relatively small ($n_s - n_a$) difference. In such a case, it is interesting to investigate the RI dispersion and the polarization of the interface region, as well as the free surface energy.

The obtained RI data were used to obtain the oscillator ($E_o$) and the dispersion ($E_d$) energies, as well as the Sellmeier dispersion coefficients ($s$) and ($\lambda_s$). According to [7], we have the following relations:

$$n^2=1+\frac{E_d E_0}{E_0^2-\hbar^2\omega^2}\ \text{(Wemple and DiDomenico),}$$

$$n^2=1+\frac{s\lambda^2}{\lambda^2-\lambda_s^2}\ \text{(Sellmeier)} \qquad (5)$$

where $\hbar$ is Planck's constant/2π, ω is the angular frequency, and $\lambda$ the wavelength.
The obtained values are given in Table 2:

*Table 2. Sellmeier and Wemple and DiDomenico coefficients. Note: The indexes "a" and "s" are for RI $n_a$ and $n_s$ used for dispersion coefficient calculations.*

| Sample | | Dispersion coefficients | | | |
|---|---|---|---|---|---|
| | | Sellmeier | | Wemple and DiDomenico | |
| | | $s$ | $\lambda_s$, nm | $E_0$, eV | $E_d$, eV |
| Gelatine, non-hardened | a | 1.242 | 181.78 | 9.43 | 11.70 |
| | s | 1.239 | 186.30 | 9.20 | 11.39 |
| Gelatine, hardened | a | 1.275 | 149.31 | 11.48 | 14.63 |
| | s | 1.287 | 142.64 | 12.01 | 15.46 |
| Styrenic A-18 μm | a | 1.248 | 67.31 | 25.46 | 31.76 |
| | s | 1.299 | 66.37 | 25.82 | 33.54 |
| Styrenic A-10 μm | a | 1.245 | 67.38 | 25.43 | 31.66 |
| | s | 1.262 | 113.54 | 15.09 | 19.04 |

In order to elucidate the substrate-hardened gelatine influence, the polar and dispersion components of the free surface energy of the substrate and gelatine layer were determined.

Owens and Wendt [8, 9], and independently of them Kaelble and Uy [10], proved that the total surface energy of a solid $\gamma_s$ can be expressed as the sum of contributions from different inter-molecular forces at the surface. Thus, the free surface energy $\gamma_s$ and polarity $p$ of the solid can be expressed as:

$$\gamma_s=\gamma_s^d+\gamma_s^h \qquad p=\frac{\gamma_s^h}{\gamma_s} \qquad (6)$$

where the superscript $d$ refers to the non-polar London-dispersion force component and h to the polar force component which includes dipole-dipole interactions, dipole-induced dipole interactions, hydrogen bonds, π bonds, charge transfer interactions, etc. The dispersion $\gamma_s^d$ and polar $\gamma_s^p$ force components can be determined from the contact angle, $\theta$, data for polar and non-polar liquids with known dispersion $\gamma_{lv}^d$ and polar $\gamma_{lv}^p$ parts of their surface energy, via the equation

$$1+\cos\theta=2\sqrt{\gamma_s^d}\left(\frac{\sqrt{\gamma_{lv}^d}}{\gamma_{lv}}\right)+2\sqrt{\gamma_s^h}\left(\frac{\sqrt{\gamma_{lv}^h}}{\gamma_{lv}}\right) \qquad (7)$$

In our study, the contact angles of bidistilled water and methylene iodide were measured by the sessile drop method, proposed by Bickerman [11]. The details of the method are described in our previous paper [12].

The reversible work of the adhesion $W_a$, which is a direct measure of the free energy of interaction between a liquid and solid or two solids, can also be calculated using the Dupre relationship and its equivalents in terms of the free surface energy components [9, 13].

$$W_a=\gamma_s+\gamma_{lv}=2\left(\sqrt{\gamma_s^d\gamma_{lv}^d}\right)+2\left(\sqrt{\gamma_s^h\gamma_{lv}^h}\right) \qquad (8)$$

Table 3 gives the polar and dispersion components of the free surface energy of glass and PMMA substrates, those of hardened gelatine and $W_a$. As seen, for glass substrates which have a high polarity and work of adhesion to the gelatine, the difference ($n_s - n_a$) is positive, while for a PMMA substrate, which has low polarity and $W_a$, this difference is negative.

*Table 3. Polar and dispersion components of the free surface energy of substrates of glass, PMMA and hardened gelatine.*

| Substrate | Surface energy [erg cm$^{-2}$] | | | Pola-rity | $W_a$ [ergcm$^{-2}$] |
|---|---|---|---|---|---|
| | polar | disper-sion | Sum | | |
| PMMA | 2.83 | 32.18 | 35.01 | 0.08 | 71.1 |
| Glass | 40.41 | 23.47 | 63.88 | 0.63 | 115.5 |
| Gelatine | 30.96 | 21.36 | 52.3 | 0.59 | |

## 4. Conclusion

The results obtained in this work confirm the increase in the polymer RI at the substrate side, as well as with diminishing OP thickness. The RI change depends on the polarity of the substrate. The only exception is Styrenic A. These results should be taken into account in optical element design using thin optical polymer films.

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