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# Surface properties of PMMA films with different molecular weights

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The paper presents the results of the investigation of the surface refractive index and the contact angle analysis of poly(methyl methacrylate) (PMMA) films. The following two PMMA trademarks, Vedril (Italy) and Plexigum (Germany) with different molecular weights were used. Films of PMMA were prepared by the drop casting technique using 10 wt.% solution of PMMA in 1,2-dichlorethane. The surface refractive index was measured by the method of the disappearing diffraction pattern using a laser microrefractometer at wavelengths of 405 nm, 532 nm and 656 nm. The experimental uncertainty was $1.5\times10^{-4}$. The obtained experimental data were used for dispersion analysis following the Sellmeier and the Wemple DiDomenico one term models. The differences between the surface refractive index values of the upper and lower side of the samples (the sample-air interface and the sample-substrate one) were observed. The influence of the polymer molecular weight on the surface properties of the lower and upper film's side was estimated based on the free surface energy values, calculated with the help of the contact angle technique and the Bickermann's method. The refractive index differences observed are analyzed on the basis of the molecular refraction and the free surface energy components changes.

**Keywords:** Refractive index, Poly(methyl methacrylate), Contact angle, Molecular weight

## INTRODUCTION

Polymethylmethacrylate (PMMA) is an amorphous thermoplastic which is derived by addition polymerization of methylmethacrylate. The polymer has very good optical properties but has poor scratch resistance. It has the best transparency of commercially available plastics. PMMA is versatile material and has been used in wide range of fields and applications. It can be purchased in one of several molecular weights. The refractive index is a basic optical property of materials and its accurate value is often needed in many branches of physics and chemistry. The optical parameters of PMMA depend on its molecular structure and they can be modified in different ways [1].

Previously, the refractive index and the birefringence dependence on molecular weight are reported for polymer blend films coated on glass substrates via spin coating [2].

The aim of the present paper is to determine the influence of the polymer molecular weight on the refractive index and the surface properties of PMMA films measured on the two sides of the films – upper and lower.

## EXPERIMENTAL PROCEDURES

### *Sample preparation*

PMMA with trademarks Vedril (Italy) and Plexigum (Germany) with molecular weights $M_w$ = 115 000, and $M_w$ = 495 000 respectively were used. 10 wt.% solutions of PMMA, weighted with 0.0001 g accuracy in 1,2-dichloroethane were used to obtain films, coated by casting technique on suitably cut and cleaned rectangular glass substrates. The thickness of the films was 160 µm, measured by Mitutoyo digimatic micrometer with ± 1 µm uncertainty. The samples were dried at room conditions for 24 hours. After drying, the films were separated from the substrates. All the measurements were carried out on the upper and lower side of the samples (on the sample-air interface and the sample-substrate one).

### *Refractive index measurement*

The surface refractive index of the samples was measured by the method of the disappearing diffraction pattern using a laser microrefractometer.

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Three diode lasers generating at 405 nm, 532 nm and 656 nm wavelengths were used as light sources.

The samples were placed between a glass prism and a metal diffraction grating. To reduce the Fresnel losses the immersion oil was used as a contact liquid. At angles smaller than the critical angle the laser beam passed through a glass prism and diffracted from the metal grating. The critical angle value *($\varphi_{cr}$)* was measured in the air at a chosen wavelength, and the refractive index of the sample *(n)* was calculated by the formula:

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

where $A$ = 65° is the refraction angle of the prism and $N$ is the refractive index of the prism for the used wavelengths 1.7347 (656 nm), 1.7480 (532 nm) and 1.7880 (405 nm). In the present experiments, a rotary stage with 1 arc min resolution was used. The experimental uncertainty of the refractive index, based on $\varphi_{cr}$ and $\Delta\varphi_{cr}$, was estimated to be less than $1.5\times10^{-4}$.

## RESULTS AND DISCUSSION

For all the samples prepared by their separation from the substrate the refractive indexes of the top ($n_a$) and bottom ($n_s$) films side were measured. Table 1 presents the measured values.

The obtained refractive index values were used to obtain the oscillator *($E_0$)* and dispersion *($E_d$)* energies, as well as the Sellmeier dispersion coefficients *(s)* and ($\lambda_s$) using the following relations [3, 4]:

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

$$n^2 - 1 = \frac{s\lambda^2}{\lambda^2 - \lambda_s^2} \text{ (Sellmeier)} \qquad (3)$$

where $\hbar$ is the Planck constant, $\omega$ is the angular frequency and $\lambda$ is the wavelength.

The obtained values of the dispersion coefficients are given in Table 2.

**Table 1.** The refractive indexes of the air-film and the film-substrate interfaces.

| Sample | λ = 405 nm | | λ = 532 nm | | λ = 635 nm | |
|---|---|---|---|---|---|---|
| | $n_a$ | $n_s$ | $n_a$ | $n_s$ | $n_a$ | $n_s$ |
| Vedril | 1.5035 | 1.5045 | 1.4934 | 1.4944 | 1.4889 | 1. |
| Plexigim | 1.4958 | 1.4973 | 1.4854 | 1.4869 | 1.4806 | 1.48219 |

**Table 2.** Dispersion coefficients.

| Sample | Interface | Sellmeier | | Wemple and DiDomenico | |
|---|---|---|---|---|---|
| | | $s$ | $\lambda_s$ , nm | $E_0$ , eV | $E_d$ , eV |
| Vedril | upper | 1.191 | 94.68 | 13.10 | 15.60 |
| | lower | 1.194 | 94.60 | 13.11 | 15.65 |
| Plexigum | upper | 1.166 | 97.41 | 12.73 | 14.84 |
| | lower | 1.170 | 97.28 | 12.75 | 14.91 |

The dispersion dependences for the samples constructed by Sellmeier one-term equation are presented in Fig. 1.

Using the group contributions we can obtain the refractive index of PMMA structural unit with the following relation [5]:

$$n = 1(-CH_2-) + 2(-COO-) + 1\left(\rangle C \langle\right) = 1.475 \qquad (4)$$

which is in fair agreement with the experimental value ($n_D$ = 1.490).

According to the Lorentz-Lorenz relation after differentiation we can obtain the relation between the refractive index and the changes of the polarisability, the polymer density and the molecular weight:

$$\frac{\Delta n}{n} = \frac{(n^2-1)(n^2+2)}{6n^2}\left[\left(\frac{\Delta\alpha}{\alpha}\right) + \left(\frac{\Delta\rho}{\rho}\right) - \left(\frac{\Delta M}{M}\right)\right] \qquad (5)$$

The obtained relation confirms the obtained experimental results. Optical properties of polymers are preliminary related to the polymer chain orientation which significantly depends on the molecular weight. If we suppose that the polarizability and the density of the films, remains unchanged it becomes clear from eqn. (5) that the refractive index decreases with increase of the molecular weight.

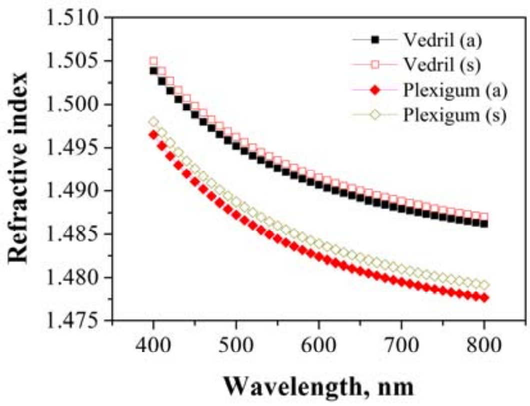


**Fig. 1.** Dispersion curves of the PMMA samples.

In order to investigate the influence of the substrate on the surface properties of the films, polar and dispersion components of the free surface energy of the upper and lower films side were obtained.

Owens and Wendt [6], and independently of them Kaelble and Uy [7], proved that the total surface energy of a solids $\gamma_s$, can be expressed as the sum of contributions from different inter-molecular forces at the surface. Thus, the free surface energy and the polarity $P$ of the solids can be expressed as:

$$\gamma_s = \gamma_s^d + \gamma_s^h \qquad P = \frac{\gamma_s^h}{\gamma_s} \tag{6}$$

where the subscript $d$ 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 $\gamma_s^P$ force components can be determined from the contact angle θ, data from polar and non-polar liquids with known dispersion $\gamma_{lv}^d$ and $\gamma_{lv}^P$ parts of their surface energy, via the equation [8]:

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

In our study contact angles of distilled water and diiodomethane were measured by the sessile drop method, proposed by Bickermann [9].

Contact angles are closely related to the wettability and the lower value of the contact angle means a greater wettability. The wettability is most often used to determine the suitability of a plastic polymer surface for bonding. Surface energy is sensitive to the chemistry of the surface, the morphology and the presence of adsorbed materials.

The obtained data is shown in Table 3.

From the data shown in Table 3 we can see that the water contact angle is less than 90° for both investigated PMMA films and the polymer surface is partially wettable. The polarity of the top films side is changed as opposed to the bottom side in both PMMA films with different molecular weights.

The free surface energy for the investigated samples is presented on Fig. 2.

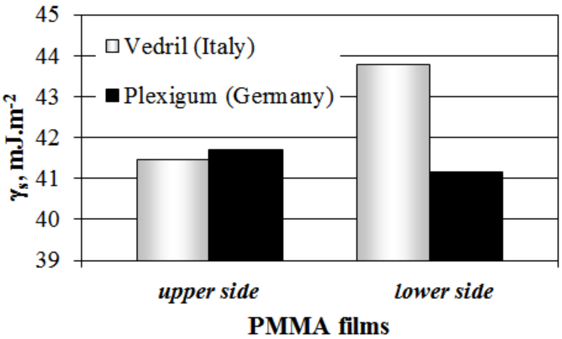


**Fig. 2.** Free surface energy for the PMMA films with different molecular weights.

As it is seen from Fig. 2 the free surface energy of the upper films side is unchanged as opposed to the lower side in both PMMA films with different molecular weights.

Table 3. Polar and dispersion components of the free surface energy of PMMA films.

| Sample | Side | $\theta_{H_2O}$ [°] | $\theta_{CH_2J_2}$ [°] | $\gamma_S^p$ [mJ.m$^{-2}$] | $\gamma_s^d$ [mJ.m$^{-2}$] | $\gamma_S$ [mJ.m$^{-2}$] | P |
|---|---|---|---|---|---|---|---|
| *Vedril* | *air* | 77.6 ± 1.5 | 39.4 ± 1.1 | 5.05 | 36.41 | 41.46 | 0.12 |
| | *substrate* | 71.2 ± 2.3 | 38.3 ± 0.6 | 7.99 | 35.81 | 43.80 | 0.18 |
| *Plexigum* | *air* | 83.8 ± 0.8 | 36.3 ± 0.7 | 2.40 | 39.30 | 41.70 | 0.06 |
| | *substrate* | 73.6 ± 1.4 | 43.2 ± 0.7 | 7.53 | 33.63 | 41.16 | 0.18 |

Surfaces with high surface energies display a strong tendency to adsorb particles (e.g. water molecules or dust particles) from the atmosphere, which leads to a reduced wettability. Therefore, contact angle measurements offer a method for studying surface aging.

## CONCLUSION

The obtained results show that the refractive index of PMMA films decreases with the polymer molecular weight increasing. The refractive index of films differs depending on the film side (upper or lower). The refractive index at the substrate side is higher than the one at the free surface side which can be attributed to the different density along the thickness of the films. These results should be taken into account in the optical elements construction.

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## ПОВЪРХНОСТНИ СВОЙСТВА НА ФИЛМИ ОТ ПММА С РАЗЛИЧНА МОЛЕКУЛНА МАСА


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(Резюме)

Статията представя резултатите от изследванията на повърхностните свойства, показателя на пречупване и контактния ъгъл на филми от ПММА. Използвани са две търговски марки ПММА, Ведрил (Италия) и Плексигум (Германия), с различна молекулна маса. Филмите са получени по метода на изливане от разтвор чрез използването на 10 wt.% разтвор на ПММА в дихлороетан. Повърхностният показател на пречупване е измерен по метода на изчезващата дифракционна картина чрез лазерен микрорефрактометър при дължини на вълната 405 nm, 532 nm и 656 nm. Експерименталната неопределеност на измерванията е $1.5\times10^{-4}$. Получените експериментални резултати са анализирани чрез дисперсионните модели на Зелмаер и Уемпъл и ДиДоменико. Констатирани са разлики в показателя на пречупване между двете страни на филма – горна и долна (контактуваща с въздуха и подложката, съответно). Влиянието на молекулната маса върху повърхностните свойства на двете страни на филма са оценени от гледна точка на стойностите на свободната енергия, изследвана по метода на контактния ъгъл, предложен от Бикерман. Разликите в показателите на пречупване са анализирани от гледна точка на приносите на молекулярната рефракция и измененията на компонентите на свободната повърхностна енергия.