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THEORETICAL PREDICTION AND EXPERIMENTAL VERIFICATION OF REFRACTIVE INDEX FOR SOME POLY METHACRYLATE POLYMERS

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ABSTRACT

In this study, we have chosen two poly methacrylate polymers viz. Poly methyl methacrylate (PMMA) and Poly ethyl methacrylate (PEMA). Polymer sample films were prepared using solution cast method and refractive index of films was measured by Abbe refractometer. Also, using chemical structure of the two polymers, refractive index values is calculated theoretically and compared with the measured values.

KEYWORDS: Refractive Index, Poly Methyl Methacrylate, Poly Ethyl Methacrylate

The interaction of light with matter results in various effects and is governed by the optical parameters of the material. The refractive index is one such fundamental property of the material and plays a crucial role in designing optical components. Refractive index is proportional to the density of the material and therefore can give information about the basic properties of the optical material.

THEORY

Refractive index is temperature dependent and density of substance also changes with temperature. So by combining refractive index and density of material in a certain way it is possible to define a temperature independent quantity, known as specific refraction 'r'. This correlation of refractive index with density was first noticed by Sir Issac Newton, in his famous work Opticks (Batsanov *et al.*, 2016) (Newton, 1721) where he remarks: "If light be swifter in bodies than in vacuo in the proportion of the sines which measure the refraction of the bodies, the forces of the bodies to reflect and refract light are very nearly proportional to the densities of the same bodies, excepting that unctuous and sulphurous bodies refract more than others of the same density" (Mathews, 1914). And mathematically is given by Laplace (Lorentz, 1915) as-

$$\frac{(n^2-1)}{\rho} = r \text{ (constant)} \qquad \text{--- (1)}$$

where ρ is material density. A better empirical form due to Gladstone and Dale (Batsanov *et al.*, 2016) (Lorentz, 1915) (Mathews, 1914) (Krevelen and Nijenhuis, 2009)

$$\frac{(n-1)}{\rho} = r \text{ (constant)} \qquad \text{--- (2)}$$

And Lorentz and Lorenz formulated the relation (Batsanov *et al.*, 2016) (Lorentz, 1915) (Mathews, 1914) (Krevelen and Nijenhuis, 2009).

$$\frac{(n^2-1)}{(n^2+2)\rho} = r \text{ (constant)} \qquad \text{--- (3)}$$

Molar refraction (R) is defined as the product of the molar mass (M) and specific refraction (r) (i.e. R = M.r) and is often used in structural chemistry (Batsanov *et al.*, 2016). Definition of molar refraction correlates refractive index with the chemical structure of the material. Various proposed definitions of molar refraction are (Krevelen and Nijenhuis, 2009).

(i) According to Gladstone and Dale (Krevelen and Nijenhuis, 2009)., molar refraction is given by (eq. 2)-

$$R_{GD} = (n-1)\frac{M}{\rho} = (n-1)V \qquad \text{--- (4)}$$

In above and following equations 'V' is specific volume.

(ii) According to Lorentz and Lorenz (Krevelen and Nijenhuis, 2009)., molar refraction is given by empirical relation (eq. 3)-

$$R_{LL} = \frac{n^2-1}{n^2+1}\left(\frac{M}{\rho}\right) = \frac{n^2-1}{n^2+1}V \qquad \text{--- (5)}$$

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(iii) Vogel (Krevelen and Nijenhuis, 2009)., proposed a very simple empirical formula, valid only at constant temperature

$$R_V = nM \qquad \text{--- (6)}$$

Goedhart studied the molar refraction values for 43 different functional groups derived from about a thousand liquid organic compounds, using an extensive regression analysis. Refractive index can be calculated using Goedhart group contribution with an average standard deviation of 0.4 % (Krevelen and Nijenhuis, 2009) (Kasarova *et al.*, 2007). We have listed some group contribution values (as required for present work) in table-1.

As refraction is additive in nature, so if we know structure of the compound then using equations (4), (5) and (6), refractive index can be estimated as -

$$n = \left(\frac{1 + 2\frac{R_{LL}}{V}}{1 - \frac{R_{LL}}{V}} \right)^{1/2} \qquad \text{--- (7)}$$

$$n = 1 + \frac{R_{GD}}{V} \qquad \text{--- (8)}$$

$$n = \frac{R_V}{M} \qquad \text{--- (9)}$$

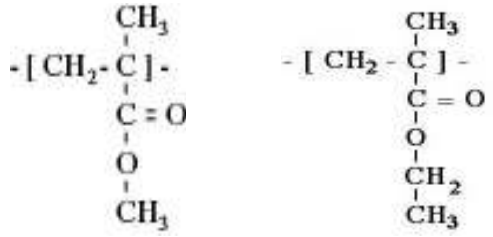
Table 1: Goedhart's value of Group contributions in 10^{-6} m^3/mol to the molar refraction (λ = 589 nm) (Krevelen and Nijenhuis, 2009)

	Groups	R_{LL}	R_{GD}	R_V
-CH3	General	5.644	8.82	17.66
-CH2	General	4.649	7.831	20.64
>C<	General	2.580	5.72	26.37
-COO-	Methyl esters	6.237	10.76	65.32
	Ethyl esters	6.375	10.94	64.49

The purpose of present work is to calculate the refractive index of PMMA and PEMA, by using their chemical structure and then to compare it with the measured value.

Refractive Index Calculation

The chemical structure of PMMA and PEMA is shown in figure- 1



(a) **(b)**

Figure 1: Chemical structure of (a) PMMA and (b) PEMA

Molar mass (molecular weight of repeat unit) of PMMA (M) = 100.12 g/mol, density (ρ) = 1.17 g/cm^3, giving specific volume V = M/ρ = 85.6 cm^3/mol. Now following, chemical structure of PMMA (fig-1a), group contributions values from table-1, and using equation (7)-

R_{LL} = 1(-CH_2-) + 2(-CH_3) + 1(-COO-) + 1(>C<)

= 1(4.649) + 2(5.644) + 1(6.237) + 1(2.580) = 24.754 cm^3/mol

Therefore value of n_D for PMMA is-

$$n_D = \left(\frac{1 + \frac{2 \times 24.754}{85.6}}{1 - \frac{24.754}{85.6}} \right)^{1/2} = 1.492$$

Using equation (8) –

R_{GD} = 1(-CH_2-) + 2(-CH_3) + 1(-COO-) + 1(>C<)

= 1(7.831) + 2(8.82) + 1(10.76) + 1(5.72) = 41.9 cm^3/mol

$$n_D = 1 + \frac{41.9}{85.6} = 1.489$$

Using equation (9) –

R_V = 1(-CH_2-) + 2(-CH_3) + 1(-COO-) + 1(>C<)

= 1(20.64) + 2(17.66) + 1(65.32) + 1(26.37) = 147.65 cm^3/mol

$$n_D = \frac{147.65}{100.12} = 1.475$$

Molar mass of PEMA (M) = 114.1 g/mol, density (ρ) = 1.119 g/cm^3, so specific volume V=M/ρ =102 cm^3/mol. Now from table 4.1, values of group contributions for PEMA

Using equation (7) and from chemical structure of PEMA (fig. 1b)-

R_{LL} = 2(-CH_2-) + 2(-CH_3) + 1(-COO-) + 1(>C<)

= 2(4.649) + 2(5.644) + 1(6.375) + 1(2.580) = 29.541 cm^3/mol

Therefore value of n_D for PEMA is-

$$n_D = \left(\frac{1 + \frac{2 \times 29.541}{102}}{1 - \frac{29.541}{102}} \right)^{1/2} = 1.491$$

Using equation (8) –

R_{GD} = 2(-CH_2-) + 2(-CH_3) + 1(-COO-) + 1(>C<)

= 2(7.831) + 2(8.82) + 1(10.94) + 1(5.72) = 49.962 cm^3/mol

$$n_D = 1 + \frac{49.962}{102} = 1.490$$

Using equation (9) –

R_V = 2(-CH_2-) + 2(-CH_3) + 1(-COO-) + 1(>C<)

= 2(20.64) + 2(17.66) + 1(64.49) + 1(26.37) = 167.46 cm^3/mol

$$n_D = \frac{167.46}{114.15} = 1.467$$

Experimental Details

Material Used: PMMA and PEMA used in this study were supplied as beads by HIMEDIA and SIGMA-ALDRICH respectively. AR grade Benzene was used as solvent for both the polymers.

Sample Preparation

The polymer sample films were prepared by well known solution casting method. Pure polymer beads (PMMA & PEMA) were dissolved separately in benzene (solvent) and the solution was cast onto glass substrate and dried for 48 hrs to form transparent films. Sample films were then peeled off from the glass substrate, with thickness ranging from 70 – 80 microns.

Measurement of Refractive Index

As per the International Standard ISO 489:1999, refractive index measurements were performed using the refractometric method. Atago's Multi-wavelength Abbe Refractometer (DR-M2) was employed to measure refractive index at 589 nm. Sample was cut in size having length of 40 mm and breadth of 8 mm. Mono bromonapthalene (1- bromonapthalene) with n_D=1.63, is used as contact liquid for the measurement. Instrument used and experimental setup for refractive index measurement is shown in figure 2.

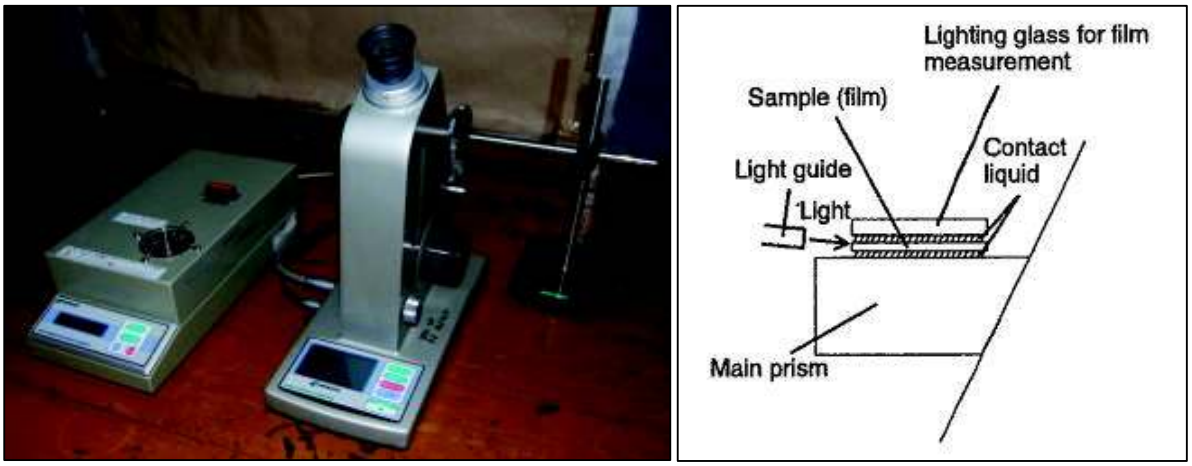


Figure 2: (a) Atago's Multi-wavelength Abbé Refractometer (Model DR-M2) (b) sample setup on main prism for refractive index measurement

Table 2: Measured, calculated and standard values of refractive indices @ 589 nm for polymer materials

Polymer Sample film	Refractive Index (n_D) value				
	Measured	Calculated from			Standard
		R_{LL}	R_{GD}	R_V	
Poly(methyl methacrylate) (PMMA)	1.4915	1.492	1.489	1.475	1.490
Poly(ethyl methacrylate) (PEMA)	1.4861	1.491	1.490	1.467	1.485

DISCUSSION AND CONCLUSION

In this paper, refractive index values of PMMA and PEMA is theoretically predicted and measured using Abbe refractometer. Measured and calculated refractive index data for two polymer samples is presented in table-2. As per the International standard ISO 489 (Plastics – Determination of refractive index), two methods are recommended for refractive index determination of plastics (optical polymers) - (1) Refractometric method i.e. a refractometer is used to measure the refractive index of the sample. Sample can be in the form of moulded parts, cast or extruded sheet, or film. This technique is applicable to both isotropic and anisotropic materials, be it transparent, translucent coloured or opaque. (2) Immersion method is recommended to determine the refractive index of powder or granulated transparent samples, using Becke line method. It is not applicable for opaque or anisotropic materials.

For present study, refractometric method i.e. multi-wavelength Abbé refractometer was used to measure the refractive index of the polymeric samples (films).

In conclusion, comparing refractive index values of PMMA and PEMA, it is clear that n_D value calculated from R_{LL} and R_{GD} is in good agreement with the measured and standard values. Whereas n_D value from R_V is quite low compare to the measured and standard values.

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