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Determination of Polyolefin Film Properties from Refractive Index Measurements

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Synopsis

A technique is described for determining the density of polyolefin film from refractive index measurements. The procedure involves the measurement of the refractive indexes (n_x, n_y, and n_z) along the three major axes of a film sample and conversion of the arithmetic average refractive index to a density value. The refractive index data are also used to calculate the per cent crystallinity and birefringence in the film.

Although the density, crystallinity, and birefringence of a polymer film can be related to its refractive index, there is little mention in the current literature of the use of the refractometer for measuring these film properties. Wiley and Hobson[1] have reviewed the ways for determining the refractive index of polymers, but the method still seems to be used infrequently. Harrison et al.[2] measured changes in refractive index to study the solid transitions in commercial paraffin waxes. More recently, Meyer and Vernon[3] used the variation of the index of refraction to analyze monomer–polymer solutions.

There are two advantages for measuring the refractive index to study film properties. The first is speed of determination. Whereas density determinations in density-gradient columns take up to 24 hr., only about 2 min. are required to obtain the refractive index data necessary for calculating a film density. This rapidity of measurement allows one to follow the early rapid changes in density (see Fig. 1) such as occur after a polymer is chill roll cast into film. The density change from 0.8835 to 0.8855 shown in Figure 1 as occurring during the first 2 hr. of aging could not be measured in a density-gradient column. The second advantage lies in the fact that the data obtained in measuring the film density can be used to determine the per cent crystallinity and birefringence of the sample.

This paper describes the procedure for obtaining the refractive index data necessary for determining the density, per cent crystallinity, and birefringence of thin polyolefin films. The methods are also applicable to other polymers.

EXPERIMENTAL

The refractive indexes of a number of chill roll-cast polypropylene film samples (0.5–1 mil thick) were determined by using a Bausch and Lomb

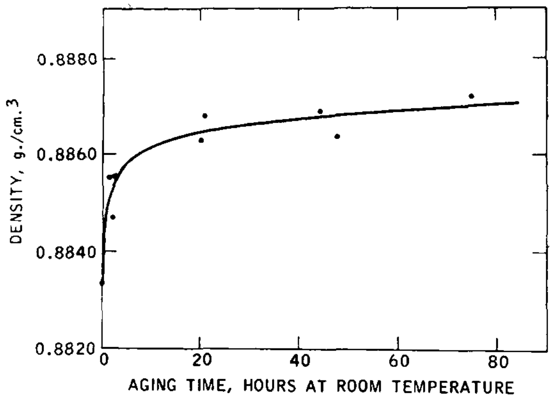

Fig. 1. Change of density during aging of polypropylene film.

Abbe-3L refractometer. The test samples included both oriented and unoriented films as well as annealed and unannealed films. Experiments with Abbe refractometers made by different manufacturers indicated that the sharpness of the line between the dark and light portions of the refractometer field is dependent on the type of instrument and method of mounting the specimen in each instrument. On the Bausch and Lomb Abbe-3L refractometer the sharpest line was obtained with transmitted light when the film sample was attached to the refracting prism without a contacting liquid or for films having rough surfaces with only a trace of contacting liquid. Sufficient contacting liquid was then placed between the illuminating prism and sample to give good light transmission. Any inert liquid having a higher index of refraction than the film sample can be used as the contact liquid. Methyl salicylate was used for this work. The sharpness of the line using the above mounting technique was equivalent to the sharpness obtained with a liquid sample.

If a polymer film is isotropic, only one determination of the index of refraction is necessary for correlation with the density, while for anisotropic films the average of the indexes of refraction n_x, n_y, and n_z along the mutually perpendicular principal axes (x, y, z) must be determined. Since the polyolefin films used were anisotropic, the refractive index along the x, y, and z axes was determined. In commercial film the x axis corresponded to the machine direction (M.D.), the y axis corresponded to the transverse direction (T.D.), and the z direction corresponded to the direction perpendicular to the film surface. The technique for determining n_x, n_y, and n_z was described by Wilchinsky and Mercier[4] and is based on the use of a polaroid disk at the refractometer eyepiece to allow passage of only the x, y, or z electric vectors, thus allowing measurement of the refractive index in the x, y, or z directions.

To measure n_x and n_z, the film sample was mounted on the refracting prism so that x axis (M.D.) was perpendicular to the long axis of the refracting prism. A polarizing eyepiece was attached to the refractometer and positioned so that privileged direction (P.D.) of the polarizer was parallel to the line separating the fields of the refractometer. The refractive index measured was n_x. With the polarizer so rotated that its P.D. is perpendicular to the field line, the refractive index measured was n_z. After determining n_x and n_z the film sample was remounted on the refracting prism with its machine direction parallel to the long axis of the prism. With the P.D. of the polarizer parallel to the field line the refractive index measured was n_y, and with the P.D. perpendicular to the field line the refractive index n_z was measured again.

DISCUSSION

Film Density from Refractive Index

The refractive index and density of a material are related by the Lorentz-Lorenz equation:

$$rd = (n^2 - 1)/(n^2 + 2)$$

where r is specific refractivity, n the refractive index, and d the density. Since the specific refractivity is considered to be almost independent of the state of aggregation and to change only slightly with temperature, a knowledge of the specific refractivity and refractive index at a given temperature allows the film density to be calculated at the temperature in question. The specific refractivity can be calculated from the refractive index and density at a given temperature or as was done in this work, the specific refractivity can be determined from the slope of the line obtained by plotting $(n^2 - 1)/(n^2 + 2)$ versus density. Figure 2 shows the variation of $(n^2 - 1)/(n^2 + 2)$, where $n = 1/3(n_x + n_y + n_z)$ with film density

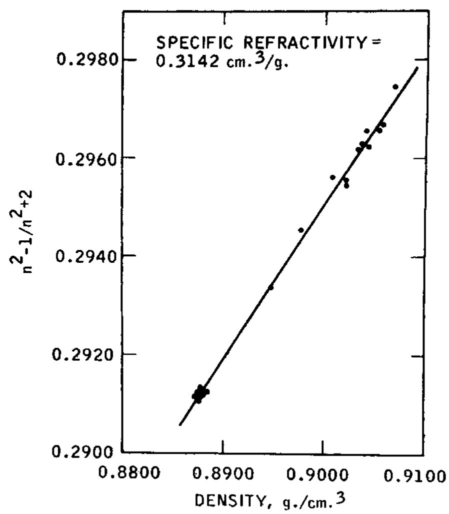

Fig. 2. Density–refractive index relation for polypropylene film.

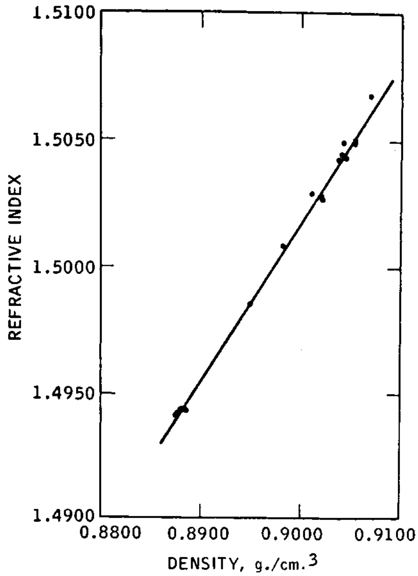

Fig. 3. Density vs. refractive index for polypropylene film.

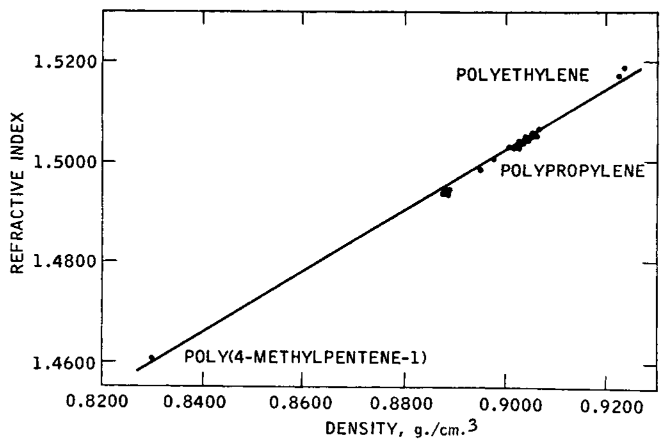

Fig. 4. Density vs. refractive index for polyolefin films.

measured by the density gradient method. For better adherence to theory the geometric mean of refractive index should be used to calculate n. A comparison of the geometric and arithmetic means showed little significant difference between the means. The specific refractivity (slope of the line in Fig. 2) was 0.3142 cm.^{3}/g.

If the average refractive index instead of $(n^2 - 1)/(n^2 + 2)$ is plotted versus density, a straight line is also obtained as shown in Figure 3. This type of plot gives a direct comparison between the two properties and facilitates the conversion of refractive index values to densities. The

Lorentz-Lorenz equation indicates that the relation between refractive index and density should be nonlinear. The apparent linearity is probably due to the fact that the line in Figure 3 is a very small segment of the total refractive index–density range which could be covered, therefore its curvature is very slight.

The refractive index versus density for polyethylene, polypropylene, and poly-4-methylpentene-1 is shown in Figure 4. The density values for the polyethylene and polypropylene were determined by the density-gradient method while literature values[5,6] were used for the density of poly-4-methylpentene-1. It can be seen that the refractive index–density relation is still linear even over the increased range of refractive index and density covered by the three polyolefins.

Crystallinity

An extension to the measurement of film density is the use of the density value for conversion to specific volume in order to determine the per cent crystallinity of film samples. Assuming an additivity of specific volumes, a crystalline density = 0.9360 g./cm.^{3}, and an amorphous density = 0.8500 g./cm.^{3},[7,8] the crystallinity (by weight) in polypropylene can readily be determined from a linear plot of per cent crystallinity versus specific volume. On the basis of the crystalline and amorphous densities given above, the polypropylene samples used in this work had a range of crystallinities of 35–55%.

Birefringence

Since the birefringence is the difference between any two refractive indexes in the film the necessary data are available from the density determination to determine three birefringence values ($n_x - n_z$, $n_y - n_z$, and $n_y - n_x$). It is generally felt that a more precise way to measure birefringence[4,9] is to determine the difference between two refractive indexes directly by an interferometric birefringence measurement. By the direct method the birefringence is given by the equation[10]

$$\Delta = \delta\lambda/2\pi d$$

where d is the sample thickness, λ the wavelength of the light and, δ the retardation. Since the sample thickness is calculated from the density and

TABLE I

$(n_x - n_y)$ (by interferometric method)	$(n_x - n_y)$ (from refractive indexes)
0.0018	0.0018
0.0049	0.0053
0.0039	0.0039
0.0026	0.0028
0.0248	0.0245

weight of a known area of film, the error introduced into the measurement is probably as great as the error arising by taking the difference between two refractive indexes. In Table I is shown a comparison of birefringence values obtained directly by an interferometric method and from the difference in refractive indexes measured with a Bausch and Lomb Abbe-3L refractometer.

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Résumé

On décrit une technique pour déterminer la densité d'un film de polyoléfine à partir de mesures de l'indice de réfraction. Le procédé comprend la mesure de l'indice de réfraction (n_x, n_y, et n_z) le long des trois axes principaux du film; on calcule ensuite la moyenne arithmétique et on la convertit en densité. A partir de ces mesures on calcule également le taux de cristallinité de la biréfringence du film.

Zusammenfassung

Eine Methode zur Bestimmung der Dichte eines Polyolefinfilms aus Messungen des Brechungsindex wird beschrieben. Der Vorgang verlangt die Messung der Brechungsindizes (n_x, n_y, und n_z) entlang der drei Hauptachsen der Filmprobe und Verwandlung des arithmetischen Mittels des Brechungsindex in einen Dichtewert. Die Brechungsindexergebnisse werden auch zur Berechnung der prozentuellen Kristallinität und der Doppelbrechung in dem Film verwendet.

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