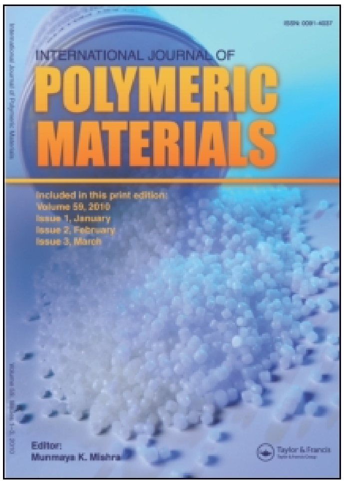

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

A Study on the Size Effect Via Spectrophotometry and Impedence Measurements

S. Saq'an[a]; A. Zihlif[b]
[a] Physics Department, University of Science and Technology, Irbid, Jordan [b] Physics Department, University of Jordan, Amman, Jordan

To cite this Article Saq'an, S. and Zihlif, A.(2007) 'A Study on the Size Effect Via Spectrophotometry and Impedence Measurements', International Journal of Polymeric Materials, 56: 4, 411 — 419

To link to this Article: DOI: 10.1080/00914030600900007

URL: http://dx.doi.org/10.1080/00914030600900007

International Journal of Polymeric Materials, 56:411–419, 2007
Copyright © Taylor & Francis Group, LLC
ISSN: 0091-4037 print/1563-5333 online
DOI: 10.1080/00914030600900007

A Study on the Size Effect Via Spectrophotometry and Impedence Measurements

S. Saq'an
Physics Department, University of Science and Technology,
Irbid, Jordan

A. Zihlif
Physics Department, University of Jordan, Amman, Jordan

The optical and dielectric properties of polycarbonate films have been studied as a function of sample thickness. The observed optical energy gaps were determined from the absorption spectra. The dielectric constant was determined from impedance data collected in the frequency range of 30 Hz–40 kHz. Four polycarbonate thin sheets of different thickness (0.17, 0.25, 0.30, and 0.55 mm) were used to assess the size effect on the physical behavior of this material. It was found that the measured properties as optical energy gap, dielectric constant, refractive index, and glass transition temperature are nearly independent of the specimen thickness. In general, it can be seen that the processing conditions of the glassy polymer sheets are quite identical and not producing structural changes leading to detectable size effect.

Keywords: dielectric constant, glass transition, optical absorption, polycarbonate, refractive index, size effect, temperature, thickness

INTRODUCTION

In some areas of technological demands the size or geometrical effect plays an important role in characterization of the physical properties

---

Received 3 July 2006; in final form 10 July 2006.

The authors thank Dr. J. Starr of the General Electric Company in USA for providing the polycarbonate sheets. Dr. S. Saq'an carried out the UV-optical measurements during his work as a visiting scientist at the "Physics of Materials Laboratory" at the University of Jordan, in Amman, Jordan.

Address correspondence to A. Zihlif, Physics Department, University of Jordan, Amman, 22110 Jordan. E-mail: adzh@ju.edu.jo

of solid state materials. It is a good tool to assess the usage of materials in specific engineering applications, especially fromthe point of component design [1]. Component design is the specification of size, shape, and configuration that will affect in-service component performance. Geometrical effects may be important in low temperature crystal physics where the value of the mean free path is limited by specimen width, and the thermal conductivity becomes a function of the dimensions of the specimen. de Haas Biermasz [2] reported that the abrupt decrease in the observed thermal conductivity of pure crystals at low temperature is caused by the size effect.

Size effects deal with variations in the values of some physical and engineering quantities, caused by stress and thermal gradients during the preparation process. These physical gradients may cause structural anisotropy and defects. Size effects may appear in thin films, processed sheets and bulk components, yet may not provide pronounced influence on materials properties. For example, the electrical resistivity, conductance, and capacitance of a thin film differ from those of the bulk material [3]. In many insulating applications, thin films are required to perform as capacitors having high dielectric constant by reducing the physical size of the capacitors. The thinner insulating material, the higher the capacitance. Tanguy [4] reported the effect of thickness on the dielectric properties of organic layers used to produce thin capacitors with high capacitance and good dielectric rigidity.

Filho and Marakani [5] studied the effects of processing and thickness on transport properties of water in glassy polycarbonate, and found that the film thickness can influence the structural organization of the original polymer. In mechanical aspect of technical materials and composites, Patron and Hashemi [6] studied the effect of specimen geometry on the fracture behavior of polycarbonate, and did not find appreciable size effect on the fracture parameters. Other researchers found that both the Poissons ratio and aspect ratio have influence on the required reinforcement. The Weibull statistical model [7–8] was successfully used to study the size effect on the mechanical behavior of glassy polymers and plastics composites. The Weibull distribution function is adequate to characterize the gauge length dependence of the test specimen. In radiation field, the projection range in solids is governed by the sample thickness, and the crystal size enhances the resolution efficiency of radiation detectors.

This article is concerned with a study aiming to assess the effect of specimen thickness on the optical energy gaps, dielectric constant, and glass transition temperature of thin sheets of glassy polycarbonate.

EXPERIMENTAL WORK

Materials

Thin sheets of Laxan polycarbonate (PC) of different thickness (0.17, 0.25, 0.30, and 0.55 mm) were used in this study. The sheets were provided by Dr. J. Starr of the General Electric Company in the United States.

Optical Absorption Measurements

Absorption spectra of thin PC sheets were measured in the wavelength range 300–600 nm (UV-visible) by means of a spectrophotometer. Absorption is expressed interms of a coefficient $\alpha(\omega)$, which is defined as the relative rate of decrease in light intensity. The absorption coefficient $\alpha(\omega)$ was calculated from the absorbance (A). After correction for reflection, $\alpha(\omega)$ was calculated using the relation:

$$I = I_o \exp(-\alpha x) \tag{1}$$

Hence

$$\alpha(\omega) = \frac{2.303}{x} \log\left(\frac{I}{I_o}\right) = \frac{2.303}{x} A(\omega) \tag{2}$$

where I_o and I are the incident and transmitted intensities, respectively, and x is the sample thickness [9–13].

Dielectric Measurements

Disc-shaped samples of different thickness and 1 cm diameter were cut from the polycarbonate sheets. The components of the dielectric constant were calculated from the measured values of impedance components: imaginary and real components. The measuring system and procedure of impedance measurements were reported elsewhere [14–16].

Differential Scanning Calorimetry (DSC)

The DSC study was carried out using Metler FP85, and melting runs were done at a heating rate of 10°C/min with nitrogen purge at flow rate of ml/min. The melting temperature of the samples were calibrated by using a standard sample of indium at the same rate. Test samples were carefully prepared and had approximately the same weight. A typical DSC scan is shown in Figure 1.

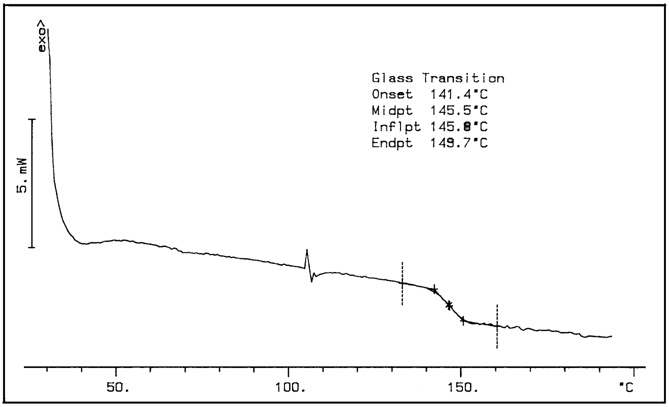

FIGURE 1 DSC scan for polycarbonate.

RESULTS AND DISCUSSION

Studying the optical absorption spectra and the dielectric behavior of polycarbonate thin sheets is helpful in assessing the effect of thickness on physical quantities such as optical energy gap, dielectric constant, refractive index, and electrical conductivity. Correlations between the determined physical parameters and the measured glass transition temperature (T_g) are useful to detect the property–thickness relationship.

Optical Results

The absorption edge of non-crystalline materials gives a measure of the band strength or energy band-gap. The relationship between energy gap, (E_g) and the position of the sharp absorption edge is:

$$E_g = hc/\lambda \tag{3}$$

where, h is Planck's constant, c is the velocity of light, and λ the wavelength. At high absorption levels, where $\alpha(\omega) > 10^4\ \text{cm}^{-1}$, the absorption coefficient for non-crystalline materials, such as glassy polycarbonate has the following frequency dependence:

$$\alpha(\omega)\hbar\omega = \beta(\hbar\omega - E_{opt})^r \tag{4}$$

where β is a constant and r an exponent which can take values of 2, 3, 1/2, and 3/2 depending on the nature of the electronic transitions (direct or indirect) responsible for optical absorption [10–13].

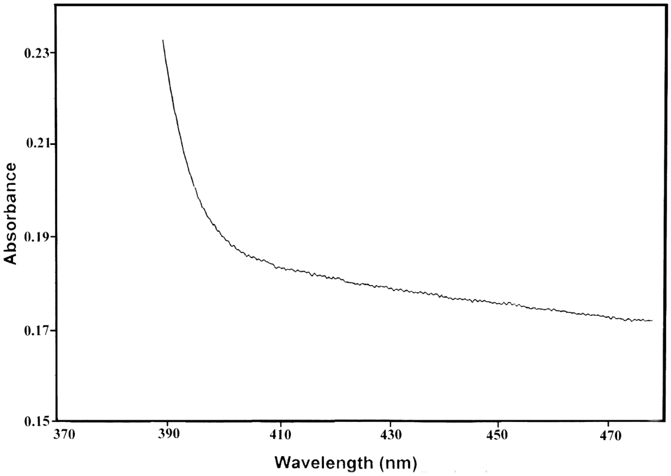

FIGURE 2 The optical absorbance spectrum of polycarbonate sheet.

Figure 2 represents the spectra of the optical absorbance (A) for polycarbonate sheet of 0.17 mm thickness. Figure 3 shows the product of the absorption coefficient $\alpha(\omega)$ and photon energy $(\alpha\hbar\omega)^2$ versus photon energy $(\hbar\omega)$ at room temperature. Extrapolation of the linear portion of this curve [11–14] gives the optical energy band gap (E_{opt}) for the glassy polymer. A good straight line is obtained with $r = 1/2$, for the four sheets. Table 1 includes the measured values of (E_{opt}) in

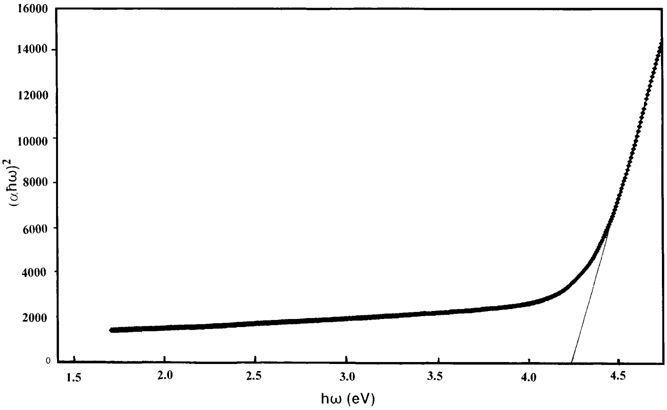

FIGURE 3 The product of optical absorption coefficient and photon energy versus the photon energy for polycarbonate sheet.

TABLE 1 Properties as Function of Thickness

Thickness (mm)	E_{opt} (eV)	ε' (1 kHz)	n	$\sigma_{AC}(10^{-12})(\Omega\cdot cm)^{-1}$	T_g (°C)
0.17	~4.2	2.88	1.70	3.4	145.4
0.25	4.21	2.98	1.70	3.4	145.5
0.30	4.21	2.92	1.71	3.5	145.3
0.55	4.23	2.95	1.72	3.5	145.5

case of direct electronic transitions as a function of sheets thickness. The table shows slight variations in (E_{opt}), which are approximately in the range of experimental errors, thus the thickness effect is very small or negligible. At low absorption levels in the range 1–10^{+4}cm^{-1}, the absorption coefficient $\alpha(\omega)$ is described by Urbach formula [10]:

$$\alpha(\omega) = \alpha_0 \exp\left(\frac{\hbar\omega}{\Delta E}\right) \tag{5}$$

where α_0 is a constant, and ΔE is the energy tail of localized states in the forbidden gap. The average value of ΔE obtained from Figure 4 is about 0.25 eV. The tailing of states at the Urbach band edge are observed in semiconductors and insulators; such tail states give contribution

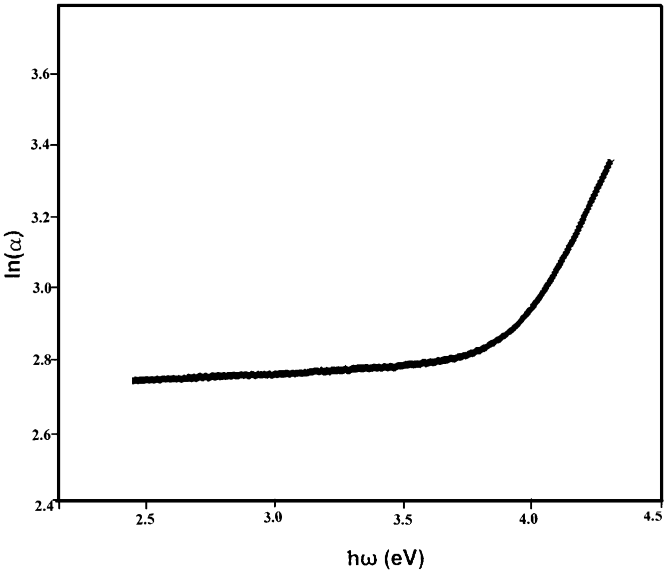

FIGURE 4 Urbach plot of Ln(α) versus the photon energy.

to optical absorption at photon energies below the band gap energy, characteristic absorption behavior in the sub-gap region [17].

Dielectric and Refractive Index Results

Dielectric spectroscopy is a useful technique for detection of small influence, caused by any physical, chemical, geometrical, and environmental factors as reported inseveral research papers presented recently in a conference on dielectric and related phenomena [18]. The real component (ε') and the imaginary component (ε'') of the dielectric constant are calculated from impedance data as were previously reported in the authors publications [9,15,19]. The values of refractive index (n) and a.c. conductivity (σ_{AC}) listed in Table 1 are calculated from the relations: $n \approx (\varepsilon')^{1/2}$, and $\sigma_{AC} = 2\pi f \varepsilon_0 \varepsilon''$ [9,15,16]. Again it can be seen that the variations observed as a function of thickness in (n) and σ_{AC} are small. The glass transition temperature T_g is an important physical parameter whose value determines the end use of an amorphous polymer as polycarbonate. It has a direct relationship with any structural changes in chain rigidity and rotation, side group, and intermolecular forces. The average measured value of T_g is about 148°C. The variations in T_g for the given PC sheets with different thickness are small as shown in Table 1, which also shows a comparison between the observed energy gap and the glass transition temperature; the constancy of both of them reflects that PC sheets have

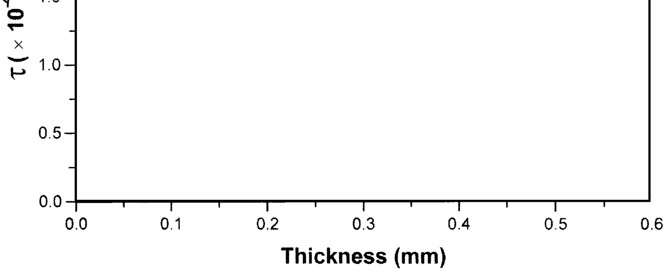

FIGURE 5 The relaxation time versus sheets thickness.

molecular regularity and isotropy. Figure 5 shows the relaxation time (τ) versus sheet thickness calculated from the Debye relation $\omega_{\max}\tau = 1$. The Debye frequency $\omega_{\max}$ corresponds to the transition peak of ε'' (or $\tan\delta$) of the observed relaxation process takes place in PC bulk under the applied electric field [9,15,17]. The figure shows that the relaxation time is about almost constant as a function of the sheet thickness. Thus, it can be seen that the determined variations in the measured physical quantities are small, or within the experimental error, a case that demonstrates that sample thickness effect has undetectable influence on the measured physical properties.

Finally, even though the spectroscopic ellipsometry studies [20] on doped transparent polymers show that their optical responses depend on the film thickness (in nanometer range), the thicker PC sheets (in millimeter range) do not show noticeable changes in the measured physical properties.

CONCLUSION

Polycarbonate sheets of different thickness were used to detect and assess the size effect on some physical quantities of this glassy polymer. It was observed in the present exercise that all examined samples have approximately the same measured physical quantities such as optical energy gaps, glass transition temperature, dielectric constants, refractive index, and a.c. electrical conductivity. The glass transition temperature and the optical energy gaps may indicate that the investigated PC sheets possess the same morphology, texture, and homogenous molecular structure. The independence of the electrical properties on thickness indicates that there is no prounced bulk and surface effects on such properties. Thus, in general, it can be concluded that there is no detectable size effect produced through the processing conditions of the examined polycarbonate sheets.

REFERENCES

[1] Callister, J. R. (1996). *Material Science and Engineering, An Introduction*, Fourth Edition, John Wiley, New York, p. 760.

[2] de Haass and Biermasz in Kittel, C. (1986). *Introduction to Solid State Physics*. Sixth Edition, John Wiley and Sons, Inc., New York, p. 121.

[3] Kroschwitz, J. I. (1988). *Electrical and Electronic Properties of Polymers*, John Wiley and Sons, Inc., New York.

[4] Tanguy, J., *J. Appl. Physics* **47**, 2792 (1976).

[5] Filho, A. and Marakani, M., *J. Macromol. Sci. Physics* **B37** (5), 627 (1998).

[6] Patron, C. and Hashemi, M., *J. Mater. Sci.* **27**, 2279 (1992).

[7] Yves, T., *J. Polym. Sci., Polym. Phys.* **33**, 147 (1995); Winsom, M., *Review: Size Effect, Composite Sci. Tech.* **59**, 1937 (1995).

[8] Abdallah, M. and Zihlif, A., *Appl. Phys. A* **60**, 437 (1995).
[9] Ahmad, M. A., Zihlif, A., Martuscelli, E., and Ragosta, G., *Polym. Composites* **13**, 56 (1992).
[10] Urbach, F., *Physics Review* **92**, 1324 (1953).
[11] Davis, E. A. and Mott, N., *Philosophy Magazine* **22**, 903 (1970).
[12] Saqa'n, S., Ayesh, A., and Zihlif, A., *Optical Materials* **24**, 629 (2003).
[13] Ramadin, Y., Zihlif, A., and Al-Ani, S. K., *Optical Materials* **5**, 69 (1996).
[14] Al-Ani, S. K., Al-Hassany, I., and Al-Dahan, Z., *J. Mater. Sci.* **30**, 3730 (1995).
[15] Eid, A., Ramadin, Y., and Zihlif, A., *Inter. Journal of Polymeric Materials* **47**, 387 (2000).
[16] Ass'ad, A. I., M.Sc. Thesis (1992). Physics Dept., The University of Jordan, Amman-Jordan.
[17] Elliott, S. R. (1998). *The Physics and Chemistry of Solids*, Wiley, Chichester, UK, Chapter 7.
[18] Papers presented in the 6th Inter. Conf.: "Dielectric and Related Phenomena," DRP (2000), Spala, Poland.
[19] Saq'an, S., Ramadin, Y., Zihlif, A., and Popovska, F., *Polymer Testing* **20**, 919 (2001).
[20] Taqatqa, O. and Al-Attar, H., *J. Optics A: Pure and Applied Optics* **5**, 8487 (2003).