

Dependence on the Spectral Scattering Coefficient on Crystallinity into Semicrystalline Polyester

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SYNOPSIS

The dependence of the spectral scattering coefficient on crystallinity into semicrystalline polyester has been performed. A simple relation, linking the crystallinity, the wavelength of light, and the scattering coefficient was obtained. It has been found that the scattering coefficient depends strongly on the crystallinity for wavelengths lower than 1 μm ; beyond 1 μm , this coefficient can be considered as independent of the crystallinity. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The optical properties of a polymer are interesting parameters for at least two reasons. The first reason is that they provide informative and convenient methods for examining the superstructure present in solid semicrystalline polymers. Thus the scattering occurs in a semicrystalline polymer because of the difference on refractive indexes of the crystalline structures (called spherulites) and of the amorphous matrix.¹ Evolution of these spectral scattering parameters gives information on the degree of crystallinity of the polymer, and it is a fact that the crystallinity determines the physical properties of the polymer material.²

The second reason is that the optical properties permit an optimization of the forming process when infrared (IR) radiations are used during the heating stage. Indeed, for special purposes (blow molding), the semifinished thermoplastic products must be brought to a thermoelastic state by supplying heat to them. IR radiation heating, generally used, has a great advantage over heating processes based on heat conduction or convection because a large part of the IR energy directly penetrates the interior of the semifinished product. The understanding and optimization of this heating stage have been extensively described elsewhere³ and are out of this pa-

per's scope. Briefly, we recall that this optimization generally requires knowledge of the temperature distributions inside the material. These temperature distributions, which depend on the IR radiation penetration inside the polymer, are functions of the spectral distribution of the emitted radiation intensity in the oven (which depends very strongly on the temperature of the radiator) and of the optical properties of the semicrystalline polymers. If, during the thermoforming process, the polymer temperature goes through the crystallization temperature range, crystallization may appear. In this case, the size and the number of spherulites change as well as the spectral scattering parameters (light scattering may occur).

The aim of this paper is to study accurately the dependence of the spectral scattering coefficient on crystallinity into a semicrystalline polyester in order to use this coefficient in a numerical simulation.

EXPERIMENTAL

Sample Preparation

To obtain different states of crystallinity,⁴ poly(ethylene terephthalate) (PET) plates (100 \times 100 mm²) of 4-mm thickness were heated in an IR crystallization oven for different time durations. Five IR lamps, 2 cm apart, were mounted on a panel in the crystallization oven. The sample was set in front of the lamps at a distance of 10 cm. The radiator temperature was 2400 K.

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The heated plates were then peeled into micro-tomic slices of 10 μm thickness. In the following sections, the depth is defined as the distance between the front surface (set in front of the lamps) and the slice of PET.

Sample Analysis

Thermal Analysis

The crystalline fraction was performed by estimation in terms of the crystallizing exotherm and melting endotherm of differential scanning calorimetry (DSC) curves. The weighted samples were heated at a constant rate of 10°C/min. The maximum of crystallinity (X_c^0) of an amorphous sample is obtained by the determination of the heat of melting ΔH_f :

$$X_c^0(\%) = \frac{\Delta H_f}{\Delta H_f^0}$$

where ΔH_f^0 is the heat of melting of a 100% crystalline polymer (140 J/g).⁵ For the semicrystalline samples, the initial crystallinity X_{ci} (before the DSC run) was obtained from the measurement of the crystallization heat (ΔH_c) on the crystallization peak recorded during the DSC run, using the following relation:

$$X_{ci} = X_c^0 \left(\frac{\Delta H_c^0 - \Delta H_c}{\Delta H_c^0} \right)$$

where ΔH_c^0 is the heat of crystallization measured on the amorphous sample.

Small-angle Light Scattering

It is well known that during crystallization, lamellar crystals typically grow from a heterogenous nucleus, at first forming a sheaf-like structure which gradually transforms to a spherically shaped structure, the spherulite. Photographic small-angle light scattering (SALS) provides a simple and rapid technique for obtaining information on crystalline structure (spherulitic, rod-like structures) and for determining the spherulite size.

Thirty years ago, Stein and Rhodes⁶ began to apply the technique of SALS to study the polymer crystalline morphology; they derived the equations for scattering from anisotropic spherulites and developed the photographic SALS method.

There are two types of geometry for SALS: the Hv geometry, when the polarizer and the analyzer are perpendicular; and the Vv geometry, when they are parallel (Fig. 1). We used the Hv scattering pattern, which contains the most useful information for spherulitic scattering. According to the model, the scattered intensities for perfect, three-dimensional, isolated spherulites in the Hv mode are given by^{7,8}

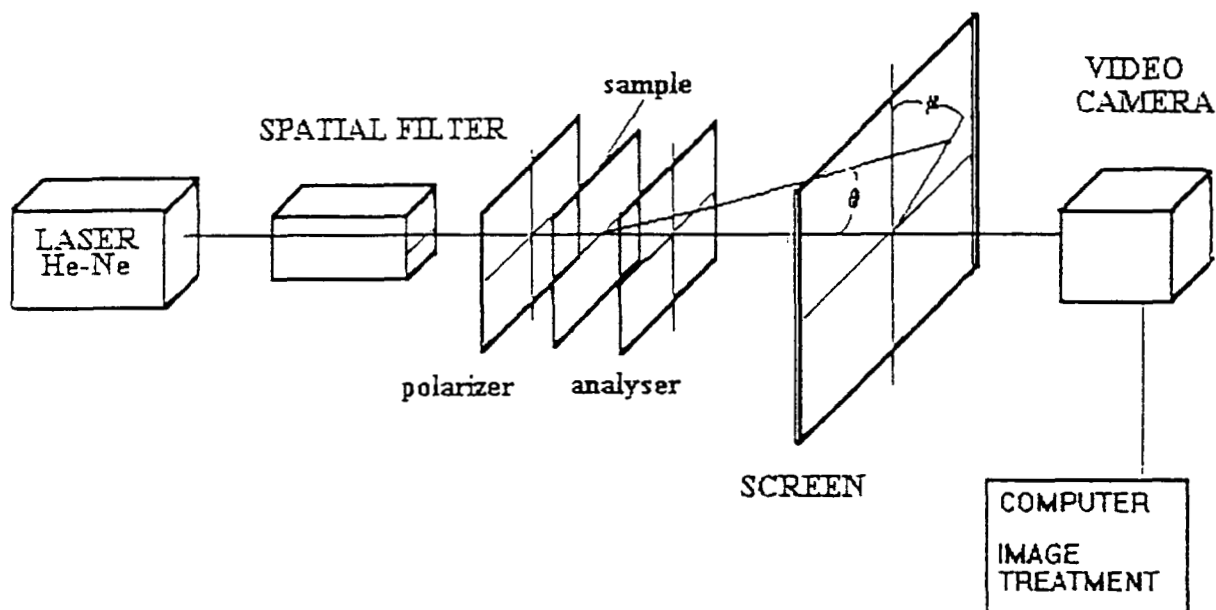


Figure 1 Schematic diagram of the SALS.

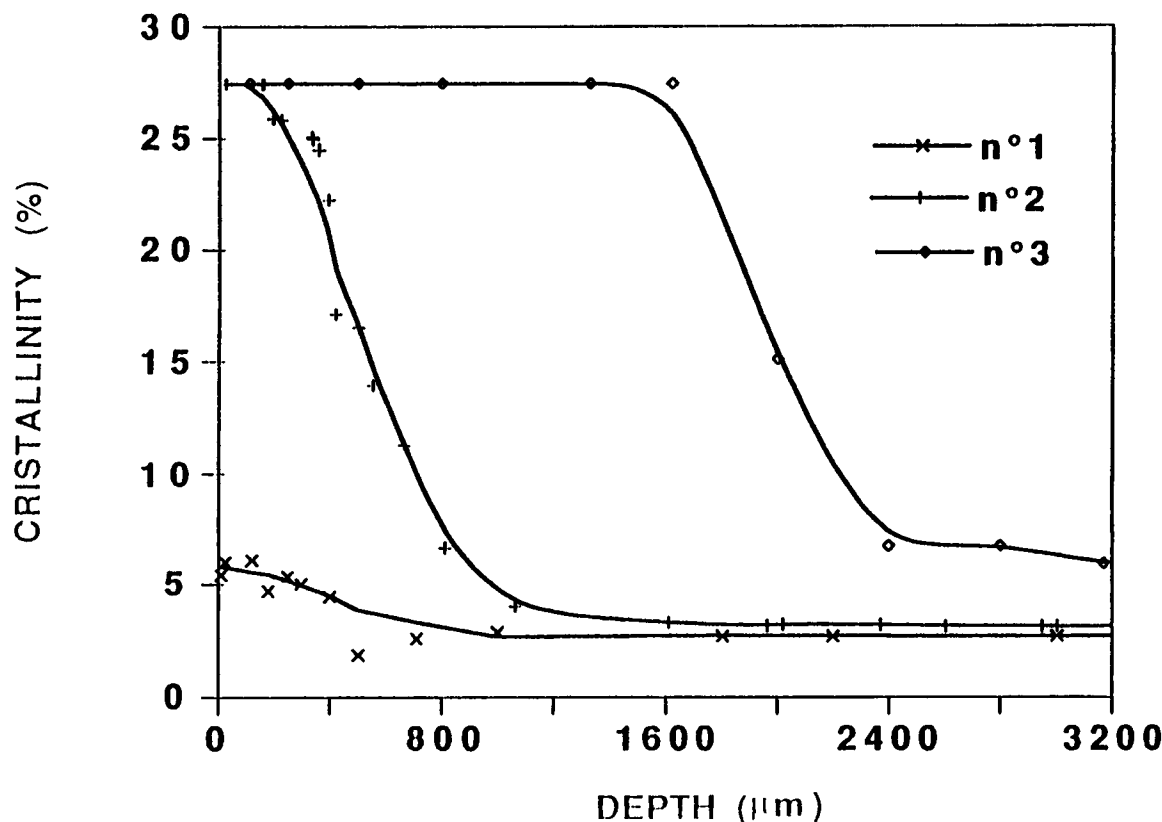


Figure 2 Crystallinity distribution in depth. Lamp temperature is equal to 2400 K. Heating time durations: n°1: 20 s; n°2: 22 s; and n°3: 25 s.

$$R_{H_v} = \frac{144\pi^4 N_s V^2}{\lambda_0^4} (\alpha_r - \alpha_t)^2 \times \left[\frac{\cos^2(\theta/2)}{\cos \theta} \sin \mu \cos \mu \cos \rho_2(\Phi_{H_v}) \right]^2$$

where R_{H_v} is the scattered intensity in Hv geometry, $U = [(4\pi R_s)/\lambda_m] [\sin(\theta/2)]$ (the shape factor), μ is the azimuthal scattering angle, θ is the radial scattering angle, R_s is the radius of the spherulite, λ_0 is the wavelength of the light in vacuum, N_s is the number of spherulites per unit volume, V is the average volume of a spherulite, α_r is the radial polarizability of the sphere, and α_t is the tangential polarizability of the sphere.

$$\cos \rho_2 = \frac{\cos \theta}{(\cos^2 \theta + \sin^2 \theta \sin^2 \mu)^{1/2}}$$

$$\Phi_{H_v} = \frac{1}{U^3} (4 \sin U - U \cos U - 3 \text{Si}U)$$

$$\text{and Si}U = \int_0^U \frac{\sin x}{x} dx$$

The maximum of R_{H_v} occurs at $U_{\max} = 4.09^9$; and

for the angle of maximum scattered intensity θ_m ; λ_m the wavelength of light in the sample can be approximated by the wavelength of light in vacuum.¹⁰ The spherulitic radius can then be deduced from the expression of the shape factor U at the maximum.¹¹

The light-scattering image is captured by a video camera and is fed to the imaging board in the computer, where it is digitalized (Fig. 1). To determine the profile of scattered intensity of the "four-leaf clover" pattern, the digitalized image placed in a frame buffer is analyzed by an image treatment. The light-scattering observation was possible with an oil immersion which minimizes the depolarization on the surface of the sample. We chose the chloro-1-naphthalene as an oil immersion rather than the aniline¹² generally used because the similarity between the refractive indices of chloro-1-naphthalene (1.65) and PET (1.64).¹³

Reflectance Measurements

The spectral scattering coefficient is determined by the albedo measurements, performed with a Beckman Acta M4 spectrophotometer fitted with an integrating sphere. The spectral range of this spectro-

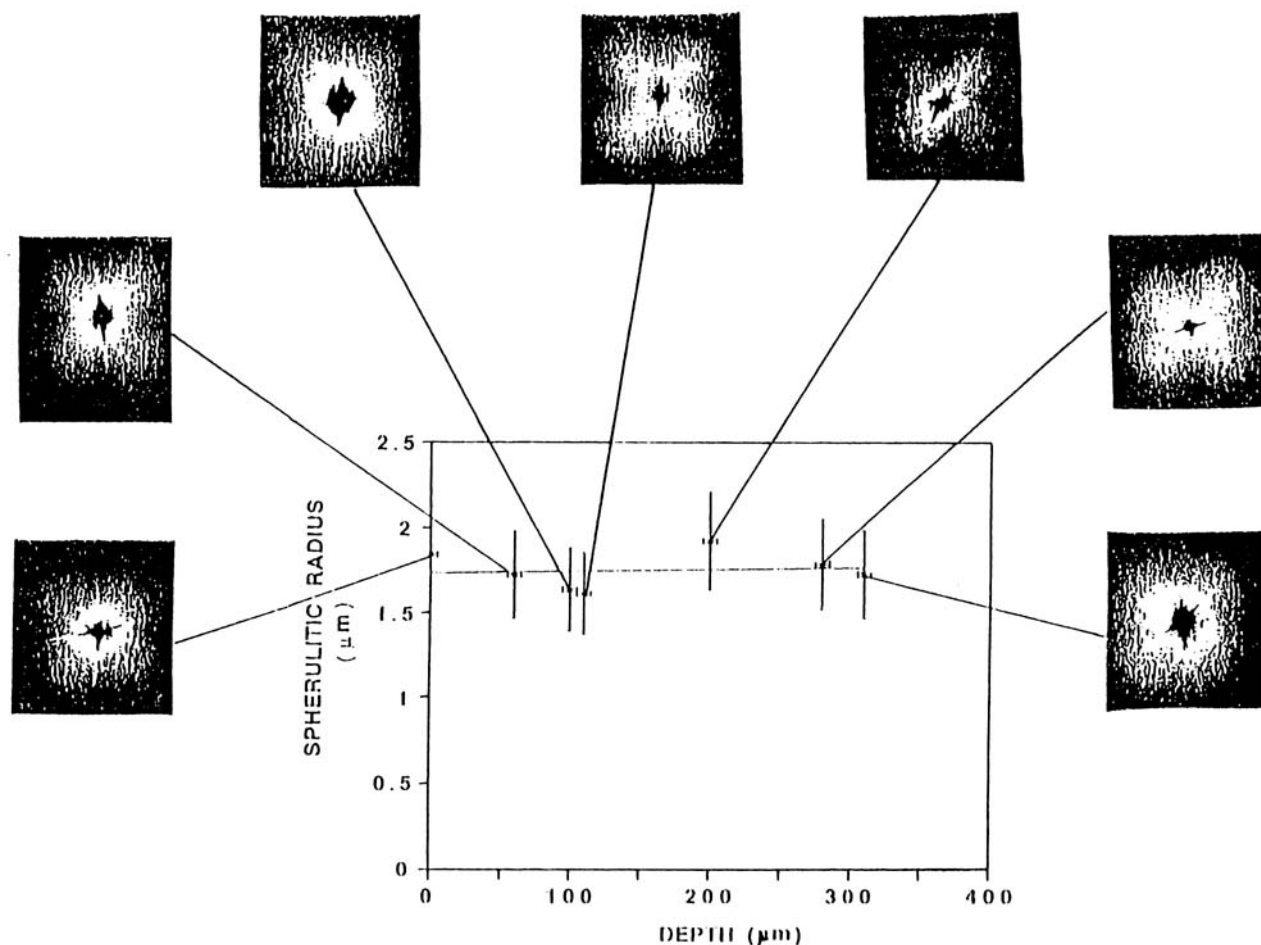


Figure 3 Evolution of the spherulitic radius in depth for the sample n°2.

photometer falls between 0.4 and 2.4 μm . The sample is mounted externally at the sample port of the integrating sphere and the total reflected radiation (reflectance) is collected and integrated by the sphere. The radiation reflected from the sample consists only of the diffuse reflection (the sample surface is tarnished to avoid the specular reflection).

To measure the evolution of the albedo with the depth in the sample, the set of data is obtained after thinning by successive abrasion of a bulky polymer. From the values of the spectral reflectance and from the spectral absorption coefficient determined for the PET,⁴ the scattering coefficient can be calculated using the following equation^{14,15}:

$$\sigma_{\lambda} = \frac{W_{\lambda}K_{\lambda}}{1 - W_{\lambda}}$$

where σ_{λ} is the monochromatic diffusion coefficient, W_{λ} is the albedo, and K_{λ} is the monochromatic absorption coefficient.

The absorption coefficient K_{λ} of a semitransparent material is a function of the wavelength of the incident radiation and of the temperature. However the variations of this coefficient with the temperature are weak,¹⁶ and we chose to neglect them.

RESULTS AND DISCUSSION

Figure 2 gives examples of the crystallinity distribution in the depth of a plate sample for different heating durations. The plates n°1, n°2, n°3 were heated, respectively, during 20 s, 22 s, and 25 s at a lamp temperature of 2400 K. For each plate, the front side (near the radiators) crystallized first; that is the reason why the maximum of crystallinity occurs on the surface. The crystallinity degree is equal to 27% for the samples n°2 and n°3, and takes the value of 6% for the sample n°1. For this sample the heating duration is too short to obtain a higher degree of crystallinity; indeed, for this lamp temper-

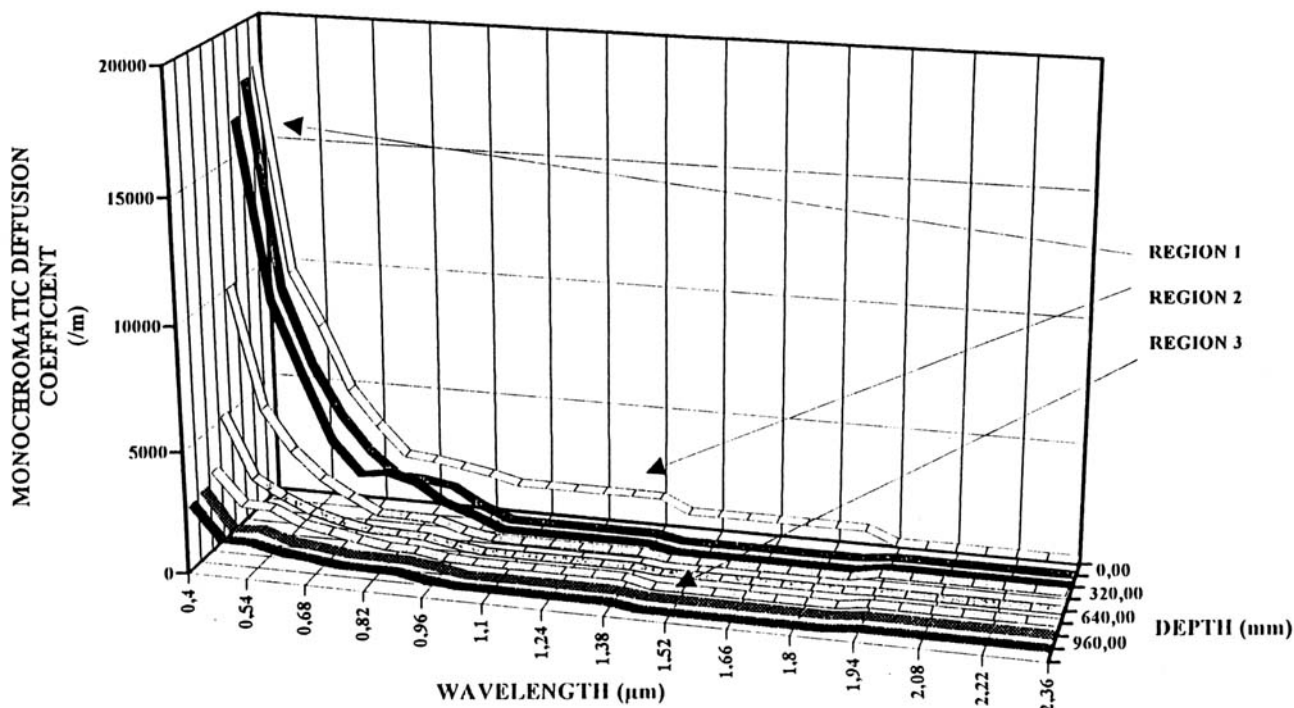


Figure 4 Variations of the monochromatic diffusion coefficient versus wavelength and depth.

ature we have measured that a completely crystallized plate needs a heating time of 33 s.

The thickness of the plate where the crystallinity reaches its maximum value increases with the time duration. Furthermore, we observed that the degree of crystallinity decreases rapidly, particularly for samples $n^{\circ}2$ and $n^{\circ}3$. This is related to the fast crystallization rate of PET in these heating conditions.^{2,17} On the back side of the plates the crystallinity, which is minimum, depends on the time duration and reaches its maximum slower than the front side (33 s vs. 22 s).

Light-scattering observation was made on the microtomic sections ($10 \mu\text{m}$) parallel to the surface of the sample. For the sample $n^{\circ}1$, Figure 3 shows the evolution of the SALS pattern versus the depth in Hv geometry and the calculated radius of spherulite. The figures can be interpreted by means of the theory of light scattering by crystalline structure, and the patterns are familiar "four-leaf clovers"¹⁰ characteristic of a spherulitic structure. The average size of the spherulites was found to be equal to $1.7 \mu\text{m}$ and does not change until the depth of $310 \mu\text{m}$. Beyond this depth, we were not able to distinguish a light-scattering pattern; that indicates the lack of completely or sufficiently developed spherulites. Indeed, according to Figure 2, the crystallinity in this depth is too low.

The spectral scattering coefficient of the sample $n^{\circ}2$, plotted in Figure 4 as a function of wavelength and depth in the sample, shows three regions: region 1: short wavelengths and low depth ($0.4 \mu\text{m} \leq \lambda \leq 1 \mu\text{m}$ and $d \leq 800 \mu\text{m}$), region 2: high wavelengths and low depth ($1 \mu\text{m} \leq \lambda \leq 2.4 \mu\text{m}$ and $d \leq 800 \mu\text{m}$), and region 3: $d > 800 \mu\text{m}$.

In region 1, we observed that the monochromatic diffusion coefficient σ_{λ} decreases rapidly when the wavelength of the incident light increases and σ_{λ} reaches its maximum observed value on the surface, for $\lambda = 0.4 \mu\text{m}$. Near $\lambda = 1 \mu\text{m}$ (region 2, $d \leq 800 \mu\text{m}$), the monochromatic diffusion coefficient depends weakly on the wavelength, and beyond $\lambda = 1.4 \mu\text{m}$ σ_{λ} can be considered as independent of the wavelength. In region 3 (depth greater than $800 \mu\text{m}$), a constant value has been measured for σ_{λ} . It is very convenient to relate σ_{λ} to the crystallinity rate. This may be done by use of the results given in Figure 2. Indeed, in this figure, instead of the depth axis it is possible to use a crystallinity axis. It is now clear that for $\lambda < 1 \mu\text{m}$ the monochromatic diffusion coefficient σ_{λ} increases when the crystallinity increases. The experimental points for different fixed wavelengths are reported in Figure 5. This figure shows a general linear behavior of σ_{λ} versus X_c . For a computing program to optimize the thermoforming process, it is necessary to obtain an analytical form of

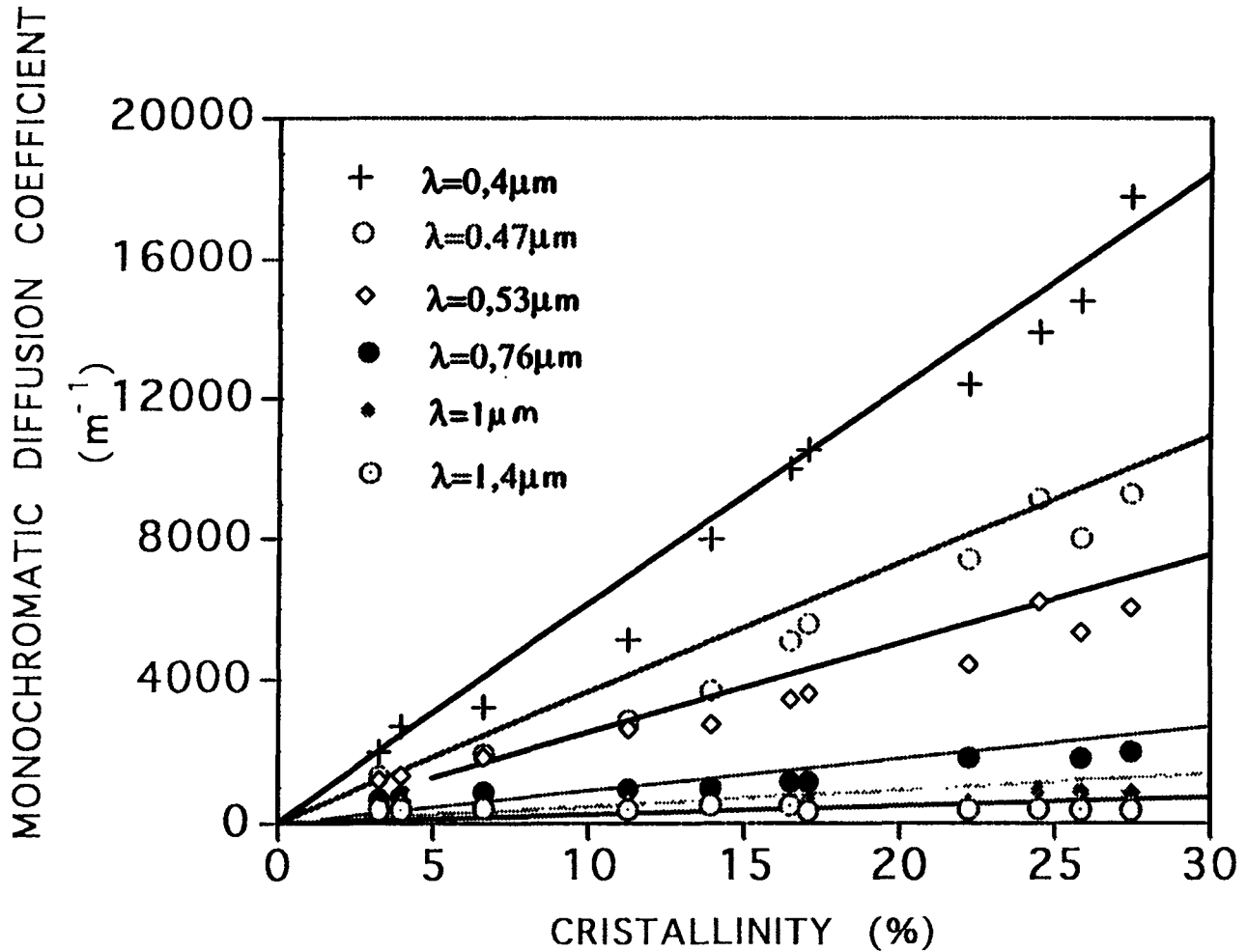


Figure 5 Variations of the monochromatic diffusion coefficient versus crystallinity. Full lines correspond to the empirical law $\sigma_{\lambda}(X_c) = (c_1 e^{c_2 \lambda} X_c / \lambda^4)$.

this behavior. The general theory of diffusion was developed by Mie¹⁸: in 1908, using the electromagnetic theory, he obtained an exact solution for the scattering of a plane monochromatic wave by an isotropic sphere of any diameter embedded in an isotropic medium. Then, the diffusion coefficient is proportional to λ^{-4} . Furthermore, it is well known that σ_{λ} depends on the degree of crystallinity X_c .³ Thus, $\sigma_{\lambda} \lambda^4 = C(\lambda) X_c$ (Fig. 5).

At a fixed wavelength, a calculation of $\sigma_{\lambda} \lambda^4$ divided by X_c gave us values of the proportional coefficient $C(\lambda)$. The variations of $C(\lambda)$ with λ could be approximated by $c_1 e^{c_2 \lambda}$.

Finally, the crystallinity dependence of σ_{λ} can be expressed by the following behavior law (full lines of Fig. 5):

$$\sigma_{\lambda}(X_c) = \frac{c_1 e^{c_2 \lambda} X_c}{\lambda^4}$$

where X_c is the degree of crystallinity, λ is the wavelength of light in micrometers, $c_1 = 7.77 \times 10^{-22}$, and $c_2 = 1.759 \times 10^6$. This approximation reveals a good agreement with the experimental values and will be used in a computing program.

For wavelengths lower than $1 \mu\text{m}$ and at a fixed wavelength, the monochromatic diffusion coefficient decreases when the crystallinity decreases. The higher values of σ_{λ} then correspond to the higher values of this crystallinity degree observed at the surface of the sample. Furthermore, we have seen that the spherulitic size determined by SALS ($1.7 \mu\text{m}$) did not change until $310 \mu\text{m}$ depth. The upper limit ($1 \mu\text{m}$) of the domain where σ_{λ} depends strongly on crystallinity and on wavelengths is comparable with the size of the spherulites. Although the dependence of σ_{λ} on X_c is very significant for a high degree of crystallinity, it exits for the lowest X_c . This is shown in Figure 6, which compares the spectral

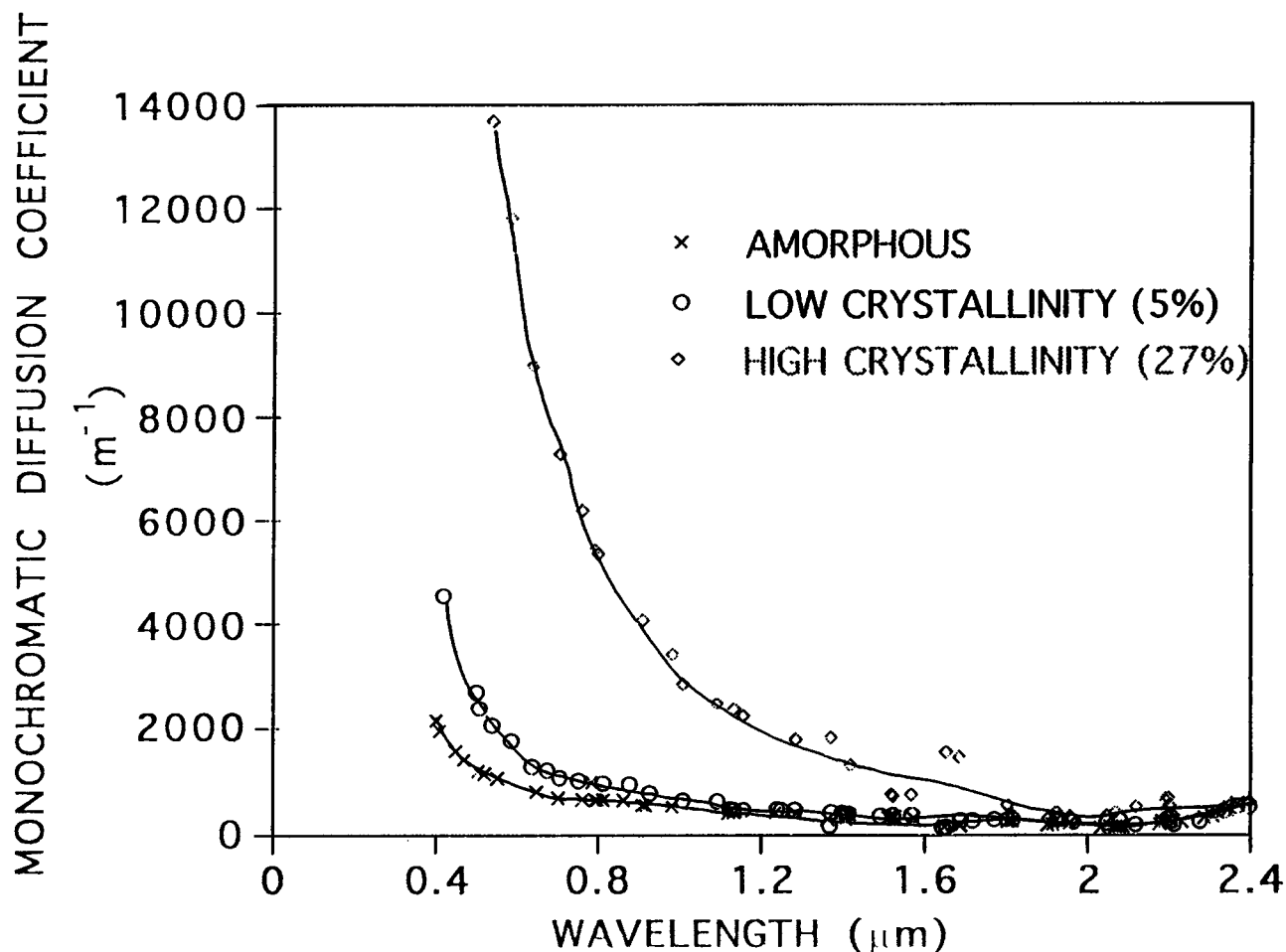


Figure 6 Comparison between amorphous, low crystallinity, and high crystallinity plates diffusion coefficient.

scattering coefficient obtained for the lowest crystallinity in the sample n°3 ($X_c = 5\%$) with the coefficient measured in an amorphous sample. It is clear that the values are different, particularly for the short wavelengths where σ_λ is higher for the low crystallinity sample than for the amorphous sample.

For wavelengths greater than $1 \mu\text{m}$, the monochromatic diffusion coefficient is no more crystallinity-dependent.

CONCLUSION

A study of the crystallinity dependence of the monochromatic diffusion coefficient has been made. We found that σ_λ depends strongly on the crystallinity for wavelengths lower than $1 \mu\text{m}$; above $1 \mu\text{m}$, σ_λ can be considered independent of X_c . For wavelengths below $1 \mu\text{m}$, the monochromatic diffusion coefficient has a linear dependence with X_c in the

prospected range of crystallinity (0–30%). Moreover, the empirical law $\sigma_\lambda(X_c)$ is in good agreement with the experimental values and will be used in a computing program for optimizing the thermoforming process, taking into account the dependence of the diffusion coefficient on the crystallinity.

Finally, we have shown that in a computing program used to optimize the thermoforming processes, it is necessary to consider the dependence of the diffusion coefficient on the crystallinity.

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