ZEUS®

TECHNICAL WHITEPAPER

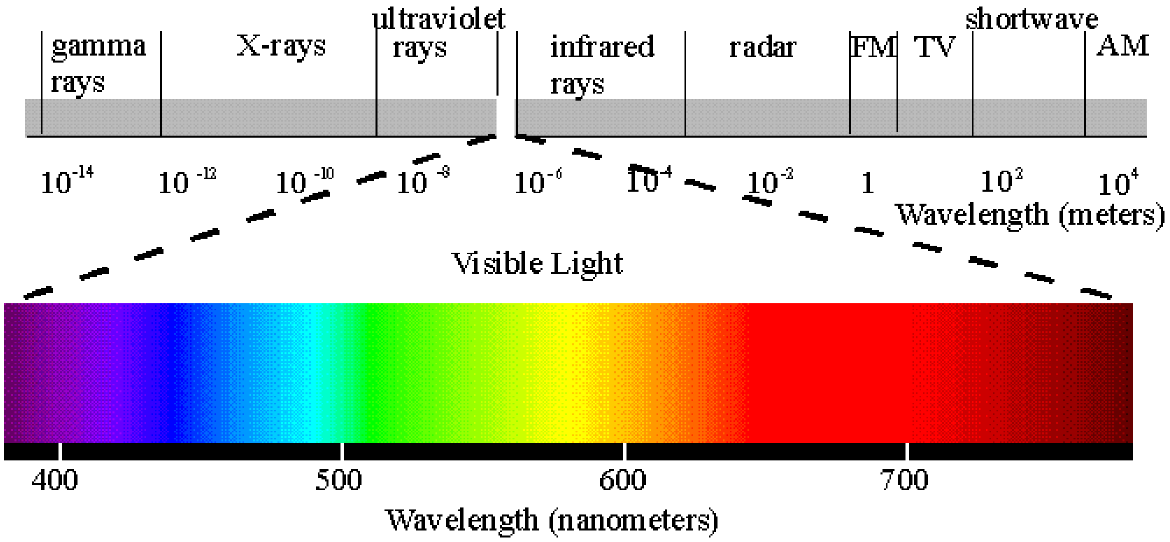
Optical Clarity of Fluoropolymers

Introduction

In a previous whitepaper (Dielectric Properties of Polymers), we discussed the dielectric properties of plastics and found that these could be related directly to the fundamental chemical structure of the basic polymer, i.e. if it was a polar or non-polar molecule. It will therefore come as no surprise to those with knowledge of physics that if the dielectric properties are directly related to the structure, then the optical properties will also be directly related to the structure of the basic polymer.

In 1873, James Clerk Maxwell showed that visible light is an electromagnetic radiation and is simply one small part of the total electromagnetic spectrum (Electricity and Magnetism: 1873).

The total electromagnetic spectrum and the visible spectrum are shown in the diagram below:



The electromagnetic and visible spectra.
The wavelength of visible light ranges from approximately 400 nm to 700 nm
(depending on the observer's eyes).

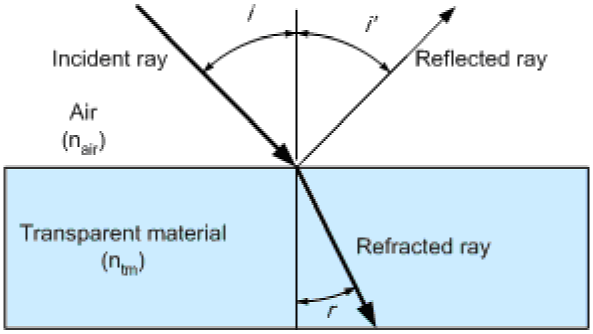
Dielectric properties and optical properties can be considered simply as responses by the polymer to different parts of the continuous electromagnetic spectrum. In fact, for non-polar plastics (such as PTFE and many other fluoropolymers, PE, PP, and PS) where only electronic polarization is present, it is possible to calculate an optical property directly from an electrical property. For these plastics the relationship is $D=n^2$ (where n = the refractive index and D = the dielectric constant).

As we have said before, understanding the structure of plastics (and in particular, the fluoropolymers) allows for an understanding of the properties at all levels.

Optical Definitions and Basics

Refractive Index

The refractive index is a measure of how much light is bent (or refracted) as it passes through a substance. It is defined by: n = sin i /sin r, where i and r are the angles of incidence and refraction respectively. The measurement of i and r are shown in the diagram below:

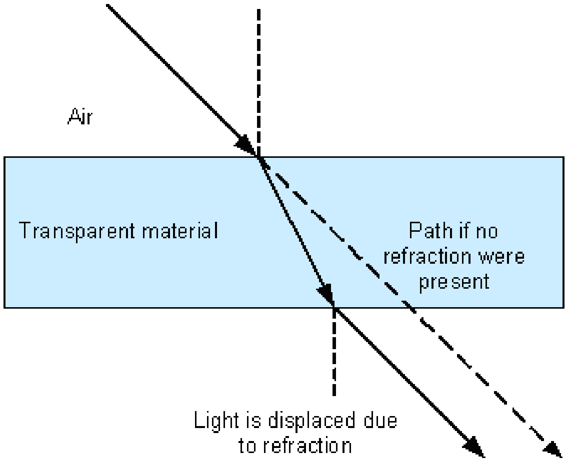


Measuring the angles of incidence and refraction

The refractive index is also the ratio of the speed of light in a vacuum to the speed in the transparent material.

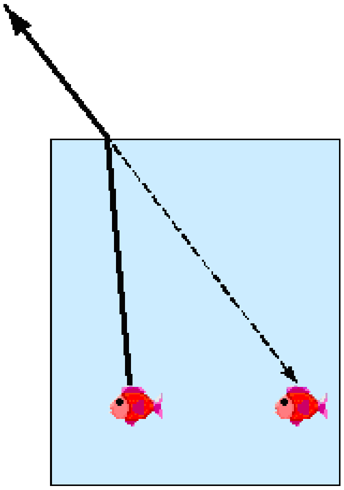
The refractive index will vary slightly with the wavelength of the light used to measure the refractive index. If ‘white’ light (a mixture of various wavelengths) is used as the incident beam, then the variation in the refractive index for the various wavelengths will lead to splitting of light into the colors of the spectrum, a process known as dispersion. To allow comparison of refractive indices for materials, the light used is generally the sodium D line (a specific wavelength).

When light enters a dense material from a less dense material then the refracted ray is bent towards the normal. When light enters a less dense material from a dense material the refracted ray is bent away from the normal. When light passes through a transparent material with parallel sides, the refractions ‘cancel out’ and the path of the light is displaced due to the presence of the transparent material. The path of light through a transparent material is shown below:



The path of light through an optically clear material due to refraction

The refractive index is one reason why ‘shooting fish is a barrel’ is not as easy as it sounds. The path of light (and therefore the image of the fish) is shown by the solid line in the drawing – the light is refracted away from the normal as it enters the less dense air from the water. If we aim at the image of the fish and the bullet follows a straight line, it will follow the dotted path and the fish will swim merrily on. The error effect gets worse as the fish is further below the surface. If you must shoot at fish in a barrel, then try to correct for refraction and aim for those closest to the surface!



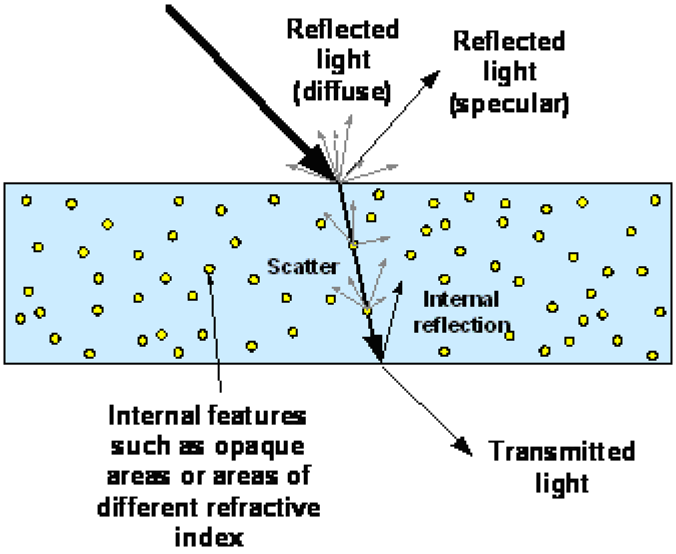
‘As easy as shooting fish in a barrel?’

Optical Clarity

The term ‘optical clarity’ is difficult to define, and the boundaries between ‘transparent’ or ‘clear’ and ‘translucent’ or ‘opaque’ are often highly subjective. What is acceptable for one observer is possibly not acceptable for another observer. It is possible to measure the degree of light transmission using ASTM D-1003 (Standard Test Method for Haze and Luminous Transmittance of Transparent Plastics), and this test method is used to evaluate light transmission and scattering of transparent plastics for a defined specimen thickness. As a general rule, light transmission percentages over 85 are considered to be 'transparent'. The perceived transparency or optical clarity is dependent on the thickness of the sample used for assessment, and the optical clarity will decrease with increasing thickness. Standard glass can be relatively optically clear in thin sections but will show a green tint (due the iron in the glass) as the thickness increases.

Optical clarity can only be achieved when the refractive index is constant through the material in the viewing direction. Any areas of opaque material (such as colorants) or areas of different refractive index, will result in a loss of optical clarity due to refraction and scattering. Optical clarity is also dependent on surface reflections from the sample. The surface reflections at the air/plastic interface create significant transmission losses. For example, PMMA's transmission loss is around 93%, and PS's is around 88%. These surface reflections can come from two basic causes: specular reflection, which is the normal reflection from a smooth surface, and diffuse reflection, which is dependent on the surface flatness of the sample. The transmission loss as a result of surface roughness or embedded particles is more often termed 'haze', and this is generally a production concern and not a property of the material. In producing blown film, haze can be caused either by melt fracture at the surface or by interfacial instability between the layers of the film.

This complex blend of surface reflections, internal scatter, and refraction is shown in the diagram below:

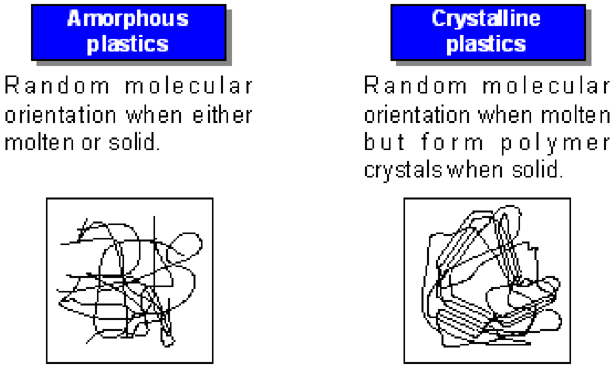


If a light ray is reflected, refracted, or absorbed during transmission then the amount of transmitted light and optical clarity will also decrease.

Optical Clarity and Polymer Types

It is possible to classify most plastics as ‘semi-crystalline’ or ‘amorphous’. Amorphous plastics have a structure of long polymer chains that are randomly oriented. When the plastic is molten, the chains slide over one another like hot cooked spaghetti, and if the plastic is cooled, the chains freeze in the random orientation (similar to cold cooked spaghetti).

Crystalline plastics are also randomly oriented in the molten state. When a crystalline plastic is cooled though, small ordered areas form to create polymer crystallites in a matrix of randomly oriented polymer chains. Polymer crystallites are small areas where the polymer chains are aligned and folded in a regular manner to form spherulites that can have a diameter of up to 0.1 mm.



Whichever type of plastic is used, the process of forming will result in flow and orientation of the long chain molecules along the direction of flow. This can result in molded-in stresses and a condition known as birefringence, where the plastic has two different refractive indices: one along the direction of flow and another across the direction of flow. Birefringence can be used to determine the degree of orientation and to visualize the flow direction to enable the flow process during mold fill...

Amorphous polymers

When no colorant has been used the amorphous plastics tend to be optically clear. Common amorphous plastics with high optical clarity are PMMA, PC, SAN, PS, and ABS, and the table below shows these ranked in terms of luminous transmittance (and therefore, optical clarity).

Polymer Family	Luminous transmittance of base polymer (%)
Optical glass	99.9
PMMA	92
PC	89
SAN	88
PS	88
ABS	79
PVC	76

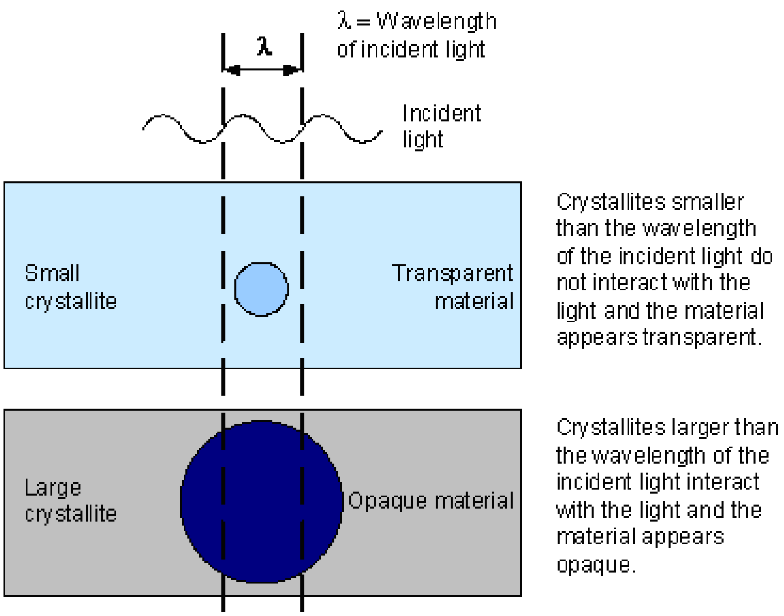
Crystalline polymers

The optical behavior of crystalline plastics is more complex because of the presence of the crystallites and their effect on the light.

- **Crystal density**
  The density of the crystalline areas is a key factor in the optical clarity of crystalline plastics because the refractive index changes with the density of the material. If the crystal density is the same or similar to that of the matrix, then the material will generally be transparent because light transmission will be unaffected by the number or size of the crystals present. For example, natural PP can be relatively transparent (but not as optically clear as amorphous plastics). If the crystal area density is much higher than the matrix density, then the size of the crystals will be the determining factor for optical clarity.

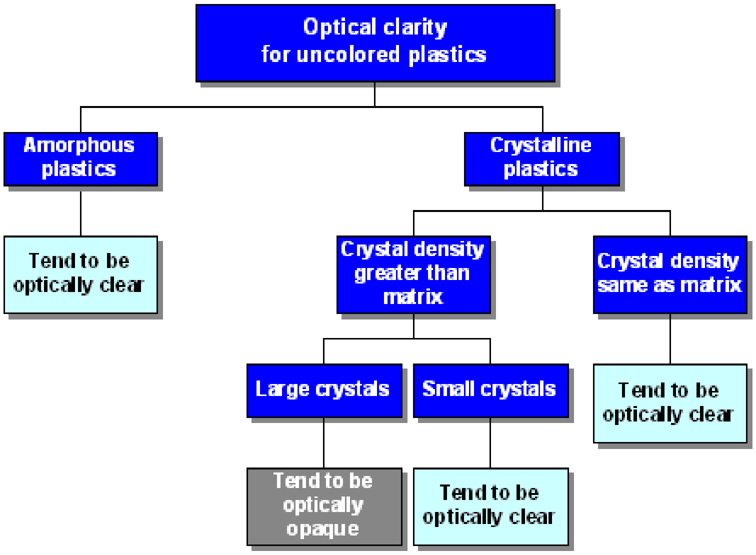
- **Crystal size**
  Visible light has a wavelength of approximately 400 to 700 nm. If the crystal areas are smaller than this range, then they do not affect the passage of light and the material can appear clear. If the crystal areas are larger, then the light will be scattered by refraction as it passes through the crystals and the material will be opaque. A spherulite with a diameter of 0.1 mm is 100,000 nm in diameter – a value significantly more than 700 nm – and this will affect the passage of light. This is the case for standard PE with normal processing, which causes it to be generally opaque at a reasonable thickness. It is, however, possible to rapidly quench PE (using chilled air in blown film production) to restrict the growth of the crystal areas to below 700 nm, and the resulting PE film will be significantly more transparent.

  Typical crystalline plastics are PA (nylon), PP, PE, POM (acetal), and PEEK™. In most cases, unless these plastics are specially treated, the optical clarity will generally be poorer than the amorphous plastics and will be appear translucent or opaque.



If the crystals are larger than the wavelength of the incident light
(crystalline density is significantly different from the matrix),
then the material will tend to be opaque.

The above discussion for uncolored polymers can be broadly summarized by the chart below:



An approximate guide to optical clarity
Note: This chart refers to the optical clarity of base polymer only.
The addition of fillers and other components (such as colors)
to the plastic can change the response to visible light.
The response to other wavelengths of the spectrum will also be different.

Optical Clarity and the Fluoropolymers

The term ‘fluoropolymers’ is a broad grouping of polymers made from monomers containing one or more fluorine atoms, or copolymers of such monomers with other monomers (see the previous Newsletter on the Chemical Resistance of Fluoropolymers). The majority of the fluoropolymers are crystalline plastics (PTFE has a very high degree of crystallinity of up to 90% in the virgin state) but some are amorphous (Teflon® AF). This range of structures means that the optical clarity of fluoropolymers can range from opaque (PTFE) to excellent (Teflon® AF has a high luminous transmittance and excellent optical clarity).

A table giving the approximate luminous transmittance of various fluoropolymers is given below.

Fluoropolymer	Luminous transmittance of base polymer(%)
Optical Glass	99.9
FEP	96
ETFE	95
Teflon® AF	95
THV	94
PFA	93
PTFE	Opaque
ECTFE	Opaque

Fluoropolymers are being actively investigated for a wide range of innovative optical applications not only because of their possible optical clarity but also because their refractive indices are generally much lower than competing materials such as PMMA and PC. The refractive index for most fluoropolymers is in the region of 1.30 to 1.45 compared with the refractive index for more traditional transparent polymers such as PMMA and PC where it is in the region of 1.5 to 1.6 (or higher). This makes the fluoropolymers suitable for optical technology products such as waveguides, optical filters, fiber gratings and a wide range of optical devices. Specialist ultra-transparent fluoropolymers are also being developed for these applications and for use in rapidly developing CMOS lithography technologies essential for the production of semiconductor devices. The optical clarity and other performance properties of fluoropolymers are opening new markets and opportunities.

Summary

Optical clarity of plastics is largely a function of the structure of the polymer (not a great surprise to regular readers of the Zeus Newsletter). Despite this it is possible to modify the structure of polymers, specifically the fluoropolymers, by controlling the degree and type of crystallinity to produce highly transparent plastics even when they would normally be opaque. Optical plastics are a growing market and the unique properties of the fluoropolymers means that they will play an increasingly critical role in a range of emerging technologies.

How Zeus Can Help

With a technical inside and outside sales force backed up with engineering and polymer experts, Zeus is prepared to assist in material selection and can provide product samples for evaluation. A dedicated R&D department staffed with PHD Polymer chemists and backed with the support of a world-class analytical lab allows Zeus an unparalleled position in polymer development and customization.

Since 1966 Zeus has been built upon the core technology of precision extrusion of high temperature plastics. Today, with a broad portfolio of engineered resins and secondary operations, Zeus can provide turnkey solutions for development and high-volume supply requirements.

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