Mie Scattering from Sphere Structures in Polymer Blends

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Synopsis

Polymer blends of transparent poly(methyl methacrylate) and polystyrene become opaque due to light scattering at the boundaries of the two polymers. The polymer blend is light brown when it is illuminated by white light. The coloring depends on the spherical domain structures existing in the polymer blend. The coloring was analyzed by using the rigorous Mie theory. The Mie results were compared with the semiempirical results previously reported by the authors. The wavelength dependence of theoretical scattering efficiencies on radii of scattering spheres from 0.05 to 1.2 μm was obtained for polystyrene spheres in poly(methyl methacrylate) matrix, and vice versa. The scattering at the short wavelength region is stronger than at the long wavelength region. The scattering efficiencies become almost constant in the visible wavelength region for sufficiently large spheres.

INTRODUCTION

Electromagnetic waves are scattered at the boundary where a change of refractive index exists. Any state of the electromagnetic wave satisfies the Maxwell equation.[1] Mie et al.[2,3] solved the equation rigorously for the scattering from a sphere of an arbitrary size and refractive index. Several approximate solutions for the equation were proposed by Rayleigh[4] and Clewell.[5]

The application of the Clewell equation to polymer blends was done by the authors for the polymer blend of poly(methyl methacrylate) (PMMA) and polystyrene (PS).[6,7] Though both polymers are transparent, the blended polymer is opaque and turns slightly brown when it is illuminated by white light. Clewell termed the coloring "structural coloring." The light scattering from polymer blends such as PMMA and PS or rubber-reinforced polystyrene was reported from the standpoint of the Debye–Bueche theory and the electromagnetic equation.[8–10] In this paper the rigorous Mie scattering theory was applied to explain the structural coloring and compared with the previous semiempirical results.

EXPERIMENTAL

The samples were composed of 97 wt-% PMMA and 3 wt-% PS. Observed by an electron microscope the samples have the following structures: the PMMA matrix contains small PS spheres (sample B) and the PS spheres contain smaller PMMA spheres (sample A). The radius distribution $N(R)$ of the inner PMMA spheres of sample A and of PS spheres of sample B counted from electron micrographs are shown in Figure 1. The absorption spectra from the ultraviolet

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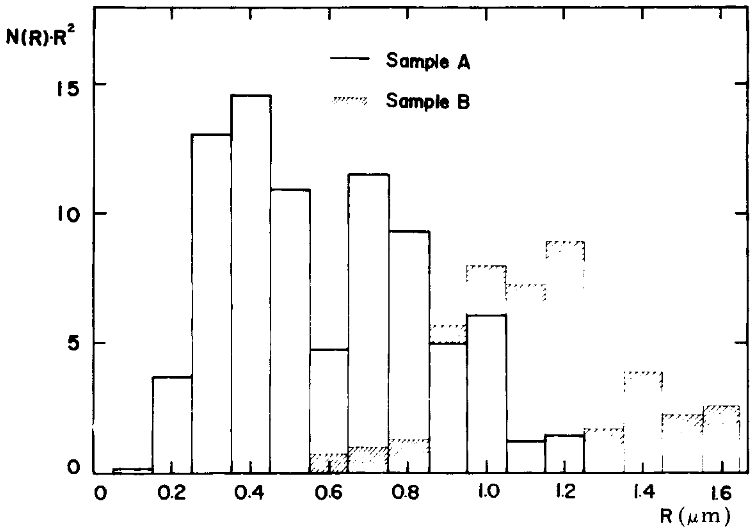

Fig. 1. Radius distributions of samples A and B. The ordinate value is $N(R)R^2$.

to the infrared region (from 300 to 2500 nm) were measured by a combination of ultraviolet, visible, and infrared spectrometers. The molecular absorption was subtracted from the spectrum by inserting a homopolymer sheet with the same thickness as the blended sample into the reference chamber of the spectrometer. Thus, the spectrum obtained shows the intensity decrease of the incident light due to the light scattering.

RESULTS AND DISCUSSIONS

The scattering efficiency $S'(\lambda,R)$ from a sphere of radius R and refractive index m_1 embedded in the medium of refractive index m_2 is obtained by Clewell semiempirically:

$$S'(\lambda,R) = \frac{[(m^2-1)/(m^2+2)]^2}{R[(0.61\,\lambda/m_2R)^2-1]^2+\{\lambda^2/m_2Ra[(m-1)^2+(1/a)]\}} \tag{1}$$

where λ is the wavelength of light in the medium, $m = m_1/m_2$, and a is a correction factor.

The rigorous Mie theory gives the scattering efficiency $S(\lambda,R)$ for the same problem:[3]

$$S(\lambda,R) = \frac{2}{x^2}\sum_{n=1}^{\infty}(2n+1)(|a_n|^2+|b_n|^2) \tag{2}$$

where

$$a_n = \frac{\psi'_n(y)\psi_n(x) - m\psi_n(y)\psi'_n(x)}{\psi'_n(y)\zeta_n(x) - m\psi_n(y)\zeta'_n(x)} \tag{3}$$

$$b_n = \frac{m\psi'_n(y)\psi_n(x) - \psi_n(y)\psi'_n(x)}{m\psi'_n(y)\zeta_n(x) - \psi_n(y)\zeta'_n(x)} \tag{4}$$

$$x = 2\pi R/\lambda, \qquad y = 2\pi mR/\lambda \tag{5}$$

and $\psi_n(z)$ and $\zeta_n(z)$ are Riccati–Bessel functions.

When there is a distribution $N(R_i)$ of sphere radii, the optical density $A(\lambda)$ at the wavelength λ due to the light scattering is expressed by eq. (6):

$$A(\lambda) = \sum_i N(R_i)\pi R_i^2 S(\lambda,R_i) \quad (6)$$

The numerical calculations of eqs. (2) to (4) were done by an IBM 1130 computer with a FORTRAN program. The computed results were in agreement with the published data by Churchill et al.,[11] in which the calculated values for m values less than unity were tabulated.

The experimental scattering curve, the calculated Mie curve (equation 6) and the Clewell curve are illustrated for sample A in Figure 2. $R_i^2N(R_i)$ was taken from Figure 1. The proportional constant was determined for the calculated curve to coincide with the experimental one at 500 nm. All curves increase rapidly at short wavelengths. The Mie curve fits the experimental curve better than the semiempirical one, especially from 300 to 500 nm and also from 1300 to 2500 nm. The difference of the optical density at 400 and 700 nm is the origin of the coloring of the blended polymer.

The same curves are illustrated in Figure 3 for sample B: the ordinate value is relative depending upon the sample thickness. The distribution of sphere radii of sample B is larger than that of sample A (Fig. 1). In this case, too, the Mie curve reproduces the experimental curve better than the Clewell curve at wavelengths shorter than 500 nm as well as longer than 1500 nm. The convex curvature at the region shorter than 900 nm in the experimental curve, which is characteristic of sample B, can be seen at wavelengths shorter than 500 nm in the Mie curve.

When the radius of the sphere is small, Clewell's semiempirical equation coincides with the Rayleigh equation and with the equation of diffraction scattering when the radius is comparable to the wavelength.[5] When the Clewell criterion is satisfied, the calculation of the light scattering becomes much simpler

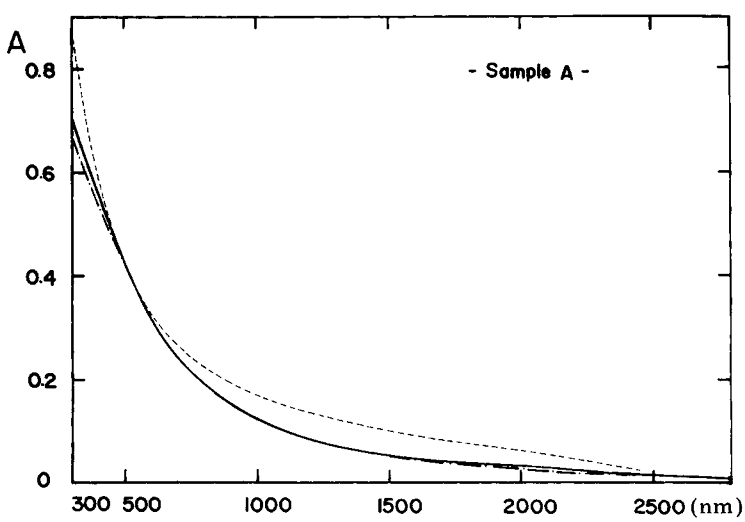

Fig. 2. Experimental (---) and calculated [Mie (—) and Clewell (-----)] curves for the optical densities of sample A vs wavelength.

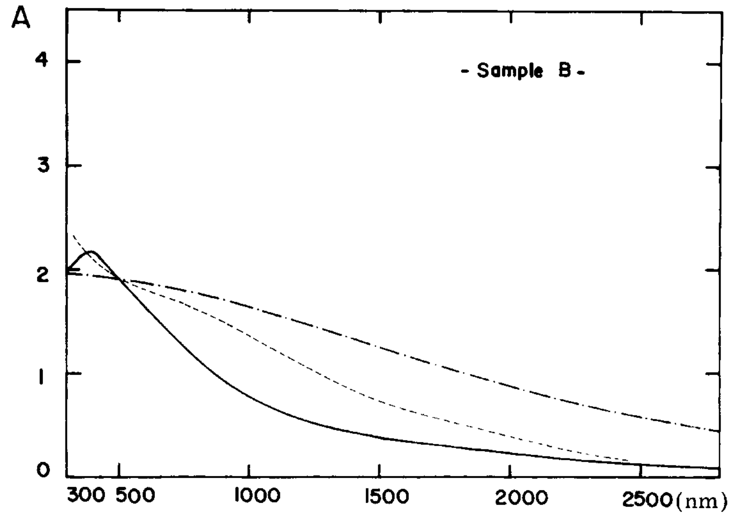

Fig. 3. Experimental (- - -) and calculated [Mie (—) and Clewell (-----)] curves for the optical densities of sample B vs wavelength.

than the calculation of the Mie series, but the equation cannot be applied exactly for the system having large radii or broad radius distribution. The scattering must be discussed according to the rigorous Mie theory in this case.

The typical scattering efficiency $S(\lambda,R)$ of eq. (2) is the ratio of the cross section for scattering to the geometric cross section of the particle (Fig. 4) for radii of 0.05 to 1.2 μm and refractive indices $m_1 = 1.60$, $m_2 = 1.49$ and $m_1 = 1.49$, $m_2 = 1.60$. When the radius is small, the scattering efficiency in the wavelengths is small. In any case, the light with short wavelength is scattered more efficiently. This is the cause of the coloring of white light after passing through small spheres. The dependence of the scattering efficiency for a large particle on the wavelength decreases and, as a result, the coloring will be reduced for a large sphere. Small particles contribute to structural coloring, whereas large particles hinder the light of all wavelengths more efficiently. At a radius of 1.2 μm, a maximum scattering intensity appears at $\lambda = 420$ nm. The maximum depends upon the particle size and refractive index. When the radius is small, both $m_1 = 1.60$, $m_2 = 1.49$ and $m_1 = 1.49$, $m_2 = 1.60$ scatterers give almost similar curves, but the former shows stronger scattering for a radius larger than 0.4 μm.

In order to discuss the light scattering more completely, multiple scattering among the spheres in the system must be considered. In the absence of multiple scattering this paper explains the phenomenon of Mie scattering fairly well. This may be due to the dilute distribution of particles in this polymer blend system.

CONCLUSIONS

The Mie scattering theory was applied to the analysis of spherical domain structures in a polymer blend which were comparable or larger in size than the wavelength of the light. The coloring of the polymer blend of PMMA and PS was interpreted by the Mie theory. When the sphere is small compared with the wavelength of the light, the use of the semiempirical light scattering equation

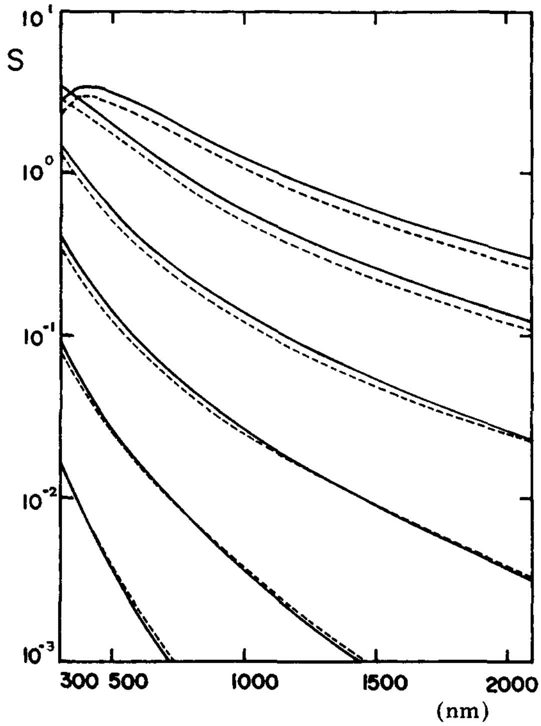

Fig. 4. Calculated scattering efficiencies S for: (—) sphere refractive index $m_1 = 1.6$ and medium refractive index $m_2 = 1.49$; (- - - - -) $m_1 = 1.49$, $m_2 = 1.6$. The radii of the spheres from bottom to top are 0.05, 0.1, 0.2, 0.4, 0.8, and 1.2 μm.

of Clewell will simplify the analysis. Such a method based upon the light scattering theory will supply a new path of polymer study, especially for determining the distribution of radii and refractive indices of scatterers and for studying the optical properties of the polymer systems.

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