OPTICS OF HETEROGENEOUS MEDIA. COMPARISON OF SOME LIGHT SCATTERING MODEL CALCULATIONS

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Dedicated to Professor Otto Wichterle on the occasion of his 80th birthday.

Typical dependences of turbidity as a function of diameter of scattering elements and their volume fractions as well as a function of the wavelength of the incident light were calculated, based both on the Lorenz–Mie theory and the fluctuation theory of Debye and Bueche. Such dependences calculated for polyethylene, polypropylene and polyamide inclusions differing slightly in their refractive index from the surrounding matrix of the same material were compared. The multiple scattering correction of the Lorenz–Mie theory based on the asymmetry factor affects the turbidity similarly as the use of mixing rule for refractive indices of multicomponent systems. A good correspondence between both theories was found only for small scattering inclusions fulfilling the approximate condition for diameter $d < 0.3\ \lambda$. Only approximate agreement of the turbidity and refractive index fluctuations up to the diameters $d < 5\ \lambda$ can be observed for the present systems using both theories. The results obtained for solid polymers were compared with model calculations for polystyrene latex under identical conditions: the latter are in a reasonable agreement with the expected trends (more pronounced dispersion and larger turbidity).

Real polymeric materials inevitably contain defects and heterogeneities of different nature and origin. They can be intrinsic, intentionally introduced or developed under mechanical stress. In any case, the presence of heterogeneities is crucial in determining important physical and technological properties. The formation of turbidity is a relatively common phenomenon that can be observed not only during mechanical loading and large plastic deformation of solid samples, but also during melt crystalization, for example in injection moulded-specimens or in phase separation processes in polymer blends. Most polymer blends are immiscible and have a distinct disperse phase. The morphology of the minority phase affects mechanical and physical properties of the blend. Optical inspection is a promising approach[1] to collecting information on polymer morphology. However, most of the light scattering approaches used for the characterization of two-phase systems or polymers deal with single light scattering process. In multicomponent systems, two other phenomena arise and complicate the single scattering picture. The first one, known as dependent scattering[2], appears when the neighbouring particles are so close that they do not scatter incident light independently. The dependent scattering is outside the scope of the present analysis and will not be considered here. The second complicating phenomenon is multiple scattering process[3]. The approach chosen to quantify this problem is based on the scattering properties of volume elements associated with the extinction efficiency factors, the asymmetry factors and phase functions of spherical particles calculated by means of the Lorenz–Mie (LM) theory[4]. This procedure is compared with simple two-phase concept where the inhomogeneity of the medium is due to two different levels of refractive indices[5].

This paper presents model light scattering calculations for polyethylene (PE), polypropylene (PP) and polyamide 6 (PA6) matrices filled with various amounts of spherical inclusions of variable diameters. Optical parameters of these inclusions are derived from the typical spherulitic structures[6] present in these polymers. It is anticipated that the refractive indices corresponding to the spherulitic structure represent the utmost possible fluctuations of refractive indices possible in such system. The calculated turbidity values (based on the LM theory[4] corrected for the multiple scattering effects[7]) are compared with the results of the Debye–Bueche (DB) fluctuation theory of light scattering in an optically heterogeneous material[5]. The purpose of the present calculations is to elucidate the effect of multiple scattering correction on the turbidity data for various volume fractions of inclusions in the material, and to test the scope of validity of the simple fluctuation theory and its parameters. The calculations are compared also with model light scattering calculations for latex dispersions with more pronounced spectral dependences of refractive indices to test the effect of refractive index dispersion on the turbidity data.

THEORETICAL

There are several possibilities of evaluating and explaining optical properties of real polymer solids. If we seek an alternative to the solution of the radiation transfer theory, considering its extreme complexity[3], often the only possibility is to make model calculations based on the assumed constituent properties. A possible approach in this respect is the use of the particle scattering theory based on the general LM approach[4] with included correction for multiple scattering[7]. Another approach consists in application of the light scattering theory based on the fluctuation concept relating transmission properties to the size and amplitude of refractive index fluctuation[5]. In this work we shall follow both approaches, giving first the necessary relations used in the evaluation.

For the light-transmission experiments reported here, the expression for the transmittance T is

$$T = I/I_0 = (1 - R)^2 \exp(-\tau l), \qquad (1)$$

where I_0, I, R, τ, and l are the incident intensity, transmitted intensity, reflectivity, turbidity, and path length, respectively. Then, the turbidity is given by[7]

$$\tau = NC_{\mathrm{sca}}(1 - \langle\cos\Theta\rangle)\,, \tag{2}$$

where N is number of spherical particles having radius R per unit volume dispersed in a nonabsorbing medium, and C_{sca} is scattering cross-section. The parameter $g = \langle\cos\Theta\rangle$, called asymmetry factor, is the average value of the scattering vector used to include the effect of multiple scattering on the turbidity values. It is the mean of $\cos\Theta$ (Θ is the scattering angle) with the angular intensity as the weighting factor, i.e.[6]

$$\langle\cos\Theta\rangle = (\pi/k^2)\int_{-1}^{+1}(i_1 + i_2)\cos\Theta/C_{\mathrm{sca}}\,\mathrm{d}(\cos\Theta)\,, \tag{3}$$

where $k = 2\,\pi/\lambda$.

When the intensity functions i_1 and i_2 are of the LM type, the asymmetry parameter g can obviously be computed from the classic LM coefficients a_n and b_n.

The alternative approach is based on the DB theoretical expression[5] for turbidity calculated using the correlation function

$$\Gamma(r) = \exp[-r/a]\,, \tag{4}$$

where a is the correlation length. The expression for turbidity can be shown to be[1]

$$\tau = 32\,\pi^4\,(a^3/\lambda_0^4)\,\langle\eta^2\rangle\,\{[(b+2)^2]/[b^2(b+1)] - 2[(b+2)/b^3]\ln(b+1)\}\,, \tag{5}$$

where

$$b = 4\,k^2\,a^2 \tag{6}$$

and the mean square value of the refractive index fluctuations is

$$\langle\eta^2\rangle = v_1\,v_2\,(n_1 - n_2)^2\,, \tag{7}$$

where v_1, v_2 are volume fractions and n_1, n_2 refractive indices of both phases. For the calculation of scattering cross-sections and corresponding turbidities we used the Mie3 program[8,9] (implementation of the LM theory) and Eq. (5). Model calculations were carried out for four systems, namely PS latex (water dispersion of PS particles) and matrices of PE, PP and PA6 with various amounts of spherical scatterers with refractive index fluctuations corresponding to a typical spherulitic structure present in these semicrystalline polymers[10]. In the case of PS latex we included in the calculation of turbidity both the effects of refractive index dispersion, i.e. the dependence of refractive index on the wavelength of light and the change in refractive index of the matrix medium due to the presence of the PS latex particles. The former effect was taken into account for both components[11]

$$n(H_2O) = 1.3244 + 3.046 \, . \, 10^{-11}/\lambda_0^2 \qquad (8)$$

$$n(PS) = 1.5683 + 10.087 \, . \, 10^{-11}/\lambda_0^2 \, . \qquad (9)$$

The concentration dependence of refractive index of the medium has a simple form of mixing rule

$$n_m = n(H_2O) + v[n(PS) - n(H_2O)] \, , \qquad (10)$$

where v is the volume fraction of PS.

The same mixing rule form has been included into calculations also for three polymer matrices with internal spherical inclusions. For the dispersion correction we used the empirical relationship developed by Cauchy[12]

$$n(\lambda) = A + B/\lambda^2 + \ldots . \qquad (11)$$

The values A and B in Eq. (*11*) for PP were determined experimentally by using selected spectral lines of Hg lamp and He–Ne laser. The effects of dispersion have been involved not only in the calculations based on the LM theory, but also in calculations of turbidity according to Eqs (*5*) and (*6*) and of $\langle\eta^2\rangle$ by means of Eq. (*7*).

RESULTS OF MODEL CALCULATIONS

In all the three solid polymer systems, monodisperse spherical inclusions of the following diameter ranges were used in the calculations of turbidities: from 0.2 to 1.0 μm with a step of 0.2 μm and from 1 to 10 μm with a step of 1 μm. The selected spectral range was 0.4 – 1.0 μm and volume fractions of minority phase 0.1, 0.2, 0.3 and 0.4. The optical parameters used in calculations are summarized in Table I. Figures 1 – 3 display the results of turbidity calculations for PE, PP and PA6 (at $\lambda = 0.6328$ μm) and illustrate the following features. First, the absolute values of turbidity reflect various amounts of optical heterogeneity as expressed by refractive index differences (cf.

Table I and Figs 1 – 3). The turbidity for a given inclusion diameter decreases from PE to PP and PA6 and approximately varies as $(n_1 - n_2)^2$, where n_1 denotes the refractive index of inclusion and n_2 is the refractive index of the corresponding polymer matrix (this approximation holds good for small d/λ ratios as discussed in more detail below). Second, the increase in turbidity due to the growing volume fractions of inclusions is saturated for volume fractions around 0.3 as known from other theoretical calculations[7,13]. The influence of growing inclusion diameters dominates over the condition of constant volume fraction and the total turbidity diminishes with increasing diameter of

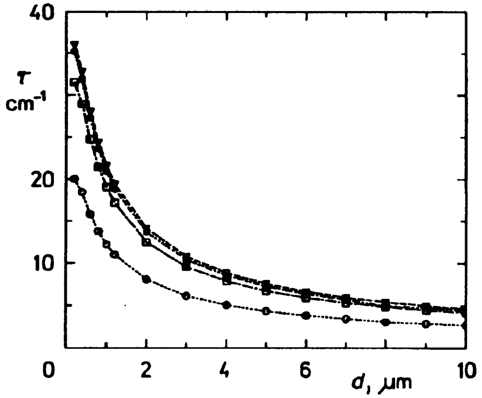

FIG. 1
PE spherical inclusions in PE matrix: Size and concentration effects on turbidity at the wavelength λ = 0.6328 μm. Volume fractions: 0.1 (O), 0.2 (□), 0.3 (∇), 0.4 (●). (For optical parameters see Table I)

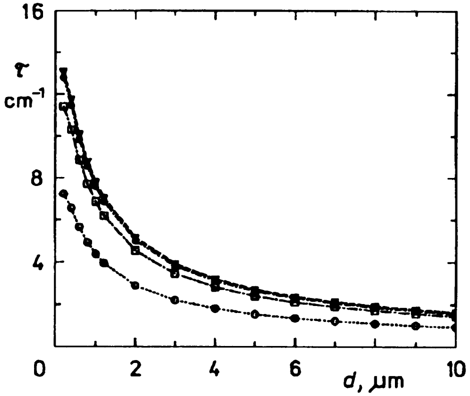

FIG. 2
PP spherical inclusions in PP matrix: Size and concentrations effects on turbidity at the wavelength λ = 0.6328 μm. Volume fraction: 0.1 (O), 0.2 (□), 0.3 (∇), 0.4 (●). (For optical parameters see Table I)

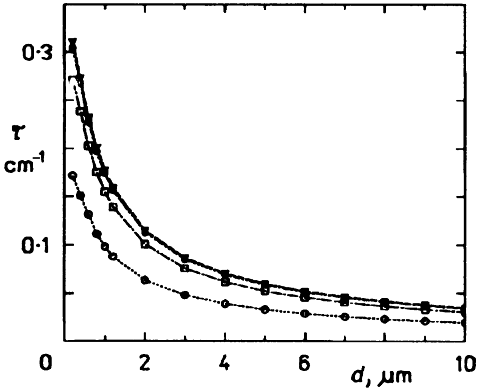

FIG. 3
PA6 spherical inclusions in PA6 matrix: Size and concentrations effects on turbidity at the wavelength λ = 0.6328 μm. Volume fractions: 0.1 (O), 0.2 (□), 0.3 (∇), 0.4 (●). (For optical parameters see Table I)

inclusion. An interesting feature of the spectral dependence is illustrated in Fig. 4, where the turbidity of PP matrix for two volume fractions of inclusions (ν = 0.1 and 0.2) is plotted for two wavelengths λ = 0.4 and 1.0 μm. The same effect of maximum turbidity around the diameter 0.4 μm was observed also for other polymer systems[14].

Now we turn our attention to the values of refractive index fluctuations as defined in Eq. (7) for two systems, PP inclusions in PP matrix and PS latex in water. We can compare the values of refractive index fluctuations, i.e. the values obtained from Eq. (7) according to the DB theory[5] with the $\langle \eta^2 \rangle^{LM}$ values based on the combination of

TABLE I
Refractive indices of spherical inclusions used in calculations (λ = 0.6328 μm)

Polymer	Volume fraction of inclusion					
	0[a]	0.1	0.2	0.3	0.4	1.0[b]
PE	1.4900	1.49663	1.50326	1.50989	1.51652	1.5563
PP	1.4710	1.47498	1.47896	1.48294	1.48692	1.5108
PA6	1.5295	1.53012	1.53074	1.53136	1.53198	1.5357

[a] Matrix; [b] inclusion.

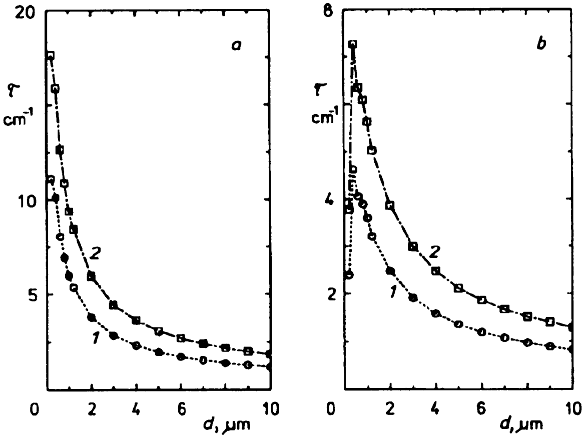

FIG. 4
Spectral and size dependence of turbidity for PP inclusions in PP. Volume fractions: *1* 0.1, *2* 0.2 ; *a* λ = 0.4, *b* λ = 1.0 μm

the LM calculation[3,4] (Eqs (*4*) and (*5*)) to test the scope of possible application of the simple relation (*7*). The spectral dependence of $\langle\eta^2\rangle^{DB}$ results from the dispersion of refractive index as expressed by Eqs (*8*) and (*9*) or (*11*). The value $\langle\eta^2\rangle^{LM}$ used for comparison was obtained from the ratio of turbidity value determined from the LM theory and that obtained from Eq. (*6*). We used the value of correlation length $a = (3/4)d$ in Eq. (*4*) in accord with the conception of correlation length for spherical particles[15].

The results of these model calculations are illustrated in Fig. 5 for the latex systems. Four volume fractions are included, 0.005, 0.01, 0.025 and 0.05. The efect of dispersion of both components (polymer/solvent, Eqs (*8*) – (*9*) or inclusion/matrix, Eq. (*11*)) and the effect of refractive index "mixing" (Eq. (*10*)) are separately plotted in Fig. 5. The symbols $\langle\eta^2\rangle^{DB}$ and $\langle\eta^2\rangle^{DBM}$ denote the use of Eq. (*7*) without and with the application of the mixing rule for refractive indices, respectively. Two other quantities plotted in Fig. 5, $\langle\eta^2\rangle^{LM}$ and $\langle\eta^2\rangle^{LMC}$ are mean-square refractive index fluctuations obtained from turbidity values calculated without and with the multiple scattering correction, respectively (Eq. (*2*) without or with the $1 - \langle\cos\Theta\rangle$ term). The values corresponding to various volume fractions of PS particles are clearly separated. In each concentration group, the order of curves from the top corresponds to the mean-square fluctuations $\langle\eta^2\rangle^{LM}$ followed by $\langle\eta^2\rangle^{LMC}$, then $\langle\eta^2\rangle^{DB}$ and last $\langle\eta^2\rangle^{DBM}$ for the wavelength $\lambda = 0.4$

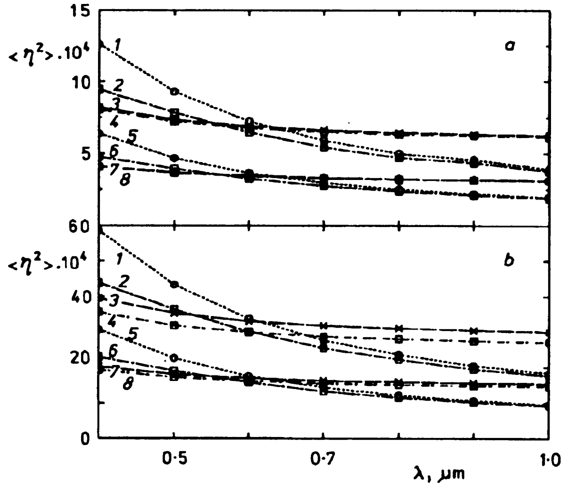

FIG. 5

Spectral and concentration dependence of mean-square refractive index fluctuations $\langle\eta^2\rangle$ for PS-water latex (particle diameter d = 0.112 μm). The $\langle\eta^2\rangle$ are: $\langle\eta^2\rangle^{LM}$ (curves *1*, *5*), $\langle\eta^2\rangle^{LMC}$ (curves *2*, *6*), $\langle\eta^2\rangle^{DB}$ (curves *3*, *7*) and $\langle\eta^2\rangle^{DBM}$ (curves *4*, *8*). Volume fraction of particles: *a* 0.005 (curves *5* – *8*), 0.01 (curves *1* – *4*); *b* 0.025 (curves *5* – *8*), 0.05 (curves *1* – *4*) μm. The values of refractive index fluctuations obtained from both approaches differ somewhat (the curves are steeper for $\langle\eta^2\rangle^{LM}$ and $\langle\eta^2\rangle^{LMC}$ calculated from the LM theory). A more detailed comparison shows that the correspondence between $\langle\eta^2\rangle^{DBM}$ and $\langle\eta^2\rangle^{LMC}$ and between $\langle\eta^2\rangle^{DB}$ and $\langle\eta^2\rangle^{LM}$ is better than for other combination of values. It appears that the mixing rule used in Eq. (7) has roughly a similar effect as the inclusion of the multiple light scattering correction in the LM calculation. It is known that PS has a very significant dispersion in comparison with PP and most of other polymers, so that one could expect a better agreement of the $\langle\eta^2\rangle^{LM}$ and $\langle\eta^2\rangle^{DB}$ values for other polymers. The results for PS/H_2O and PP inclusion/PP systems are given in Fig. 6 for the same volume fractions of the minority phase. The spectral dependences for both systems are not too different, but still the system PP inclusion/PP displays less dispersion.

It would be very useful if one could apply the simple calculation based on Eqs (5) and (7) inside the LM region. The physical explanation of the use of Eqs (5) and (7) consists in the assumption that small fluctuations coupled with long-range correlations are as effective in scattering as larger fluctuations in which the extent of the fluctuations is not so great. It is clear that this assumption is not generally valid, and the present calculations confirm the limitation. We can find a statement[1] that Eq. (5) is valid for any value of d/λ , but a closer inspection reveals that the validity of Eq. (5) is principally limited due to the use of simple phase function[6] $(1 + \cos^2\Theta)$. We tested the

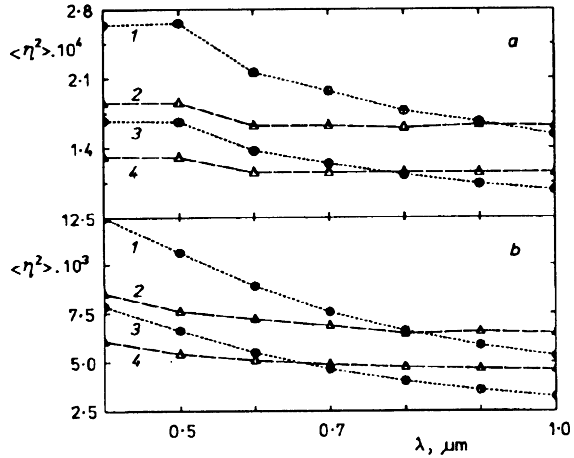

FIG. 6

Spectral and concentration dependence of mean-square refractive index fluctuations $\langle\eta^2\rangle$ for various scatterers (particle diameter d = 0.112 μm). The $\langle\eta^2\rangle$ are: $\langle\eta^2\rangle^{LMC}$ (curves *1*, *3*); $\langle\eta^2\rangle^{DBM}$ (curves *2*, *4*). Volume fraction of particles: 0.1 (curves *3*, *4*), 0.2 (curves *1*, *2*). *a* PS-H_2O latex; *b* PP inclusions in PP matrix applicability of Eqs (*5*) and (*7*) for diameters from 1 to 10 μm and volume fractions 0.1 and 0.2 in the spectral range 0.4 – 1.0 μm. It can be concluded that for diameters $d < 5\,\lambda$ the resulting scattering process can be considered as an approximate product of the value and extent of fluctuations in refractive indices as in Eqs (*5*) and (*7*). For such diameters and optical parameters of PP inclusions in PP an acceptable agreement between the values $\langle\eta^2\rangle^{LM}$ and $\langle\eta^2\rangle^{DB}$ (differing about twice) can be obtained. For larger d/λ , the use of Eqs (*5*) and (*7*) is questionable and resulting refractive index fluctuations differ by an order of magnitude. Two practical aspects that could complicate the results discussed above should be noted: the effect of particle size distribution and the effect of nonspherical scatterers. These effects can be taken into consideration by selecting a proper size distribution[13] and processing the more general form of Eq. (*2*). We do not expect principal differences using this approach, but naturally a much more complicated procedure must be performed.

The results of present calculations can be summarized as follows:

a) In spite of its relative simplicity the DB fluctuation theory (Eqs (*4*) – (*7*)) gives turbidity values in good agreement with the predictions of the LM concept (Eqs (*1*) – (*3*)), if the effects of dispersion and concentration are considered. A relatively good agreement of refractive index fluctuation values is obtained for diameters $d < 0.3\,\lambda$; only approximate validity can be expected for $d < 5\,\lambda$. Discrepances of one order of magnitude are obtained for larger diameters.

b) The correction for multiply-scattered light used in the LM calculations works effectively similarly as the application of mixing rule for the refractive indices of the two-phase systems, but gives a less steep spectral dependence of refractive index fluctuations.

c) The effect of wavelength of the light used for illumination on the absolute turbidity value is more pronounced for inclusions of small diameters (ca 0.2 – 0.4 μm) than for larger inclusions. Therefore, the polydispersity of particles could complicate the absolute turbidity values for inhomogeneous polydisperse systems in the given size range.

d) The application of the above approach to other polymer systems[14] with known optical parameters is straightforward.

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