

STRESS WHITENING IN POLYPROPYLENE. I. LIGHT SCATTERING THEORY AND MODEL EXPERIMENTS

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Dedicated to Dr Blahoslav Sedlacek on the occasion of his 70th birthday.

Theoretical background for an optical method is presented which makes it possible to distinguish unambiguously between voids and particles as light scattering sites in polymeric materials. Typical dependences of turbidity as a function of diameter of scattering elements, their volume fractions and also turbidity curves as a function of the wavelength of the incident light were calculated, based both on the Lorenz-Mie theory and the fluctuation theory. Such dependences calculated for polypropylene-containing voids on the one hand and particles, differing only slightly from the surrounding matrix in their refractive index, on the other hand, are markedly different. The most significant results are: (i) Turbidity is at least by two orders of magnitude larger for voids in comparison to embedded particles of ethylene-propylene (EPDM) rubber of the same size, concentration and at the same wavelength. (ii) The wavelength dependence of turbidity for EPDM particles and the inherent refractive index fluctuations in the polypropylene matrix is much steeper as compared to voids for all considered diameters (0.1–10 μm). Thus, the nature of stress whitening in complex polymeric materials can be determined from turbidity measurements.

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 for determining important mechanical properties such as strength and toughness. On the other hand, occurrence of defects and heterogeneities affects also optical properties of polymers. It is well known that under tensile strain many amorphous polymeric materials undergo gradual loss of optical transparency in a stress-whitening process. This is generally ascribed to voiding, specifically to the transformation of strain energy into surface energy of newly created internal voids^{1–5}. The origin of turbidity and stress whitening in semi-crystalline polymers is less unambiguous. In this case heterogeneous changes of turbidity can be observed not only during mechanical loading and large plastic deformations, but also during solidification from melt, for example in injection-moulded specimens. Consequently, light scattering behaviour can be then ascribed not

only to open voids, but also to embedded particles, such as crystallites, spherulites or (in rubber-modified polymers) to rubber particles. The origin of stress whitening in semicrystalline polymers is therefore still a matter of some controversy⁶⁻¹⁰. This paper presents theoretical background which makes it possible to unambiguously distinguish between voids and particles as scattering elements in semitransparent materials. The possibilities of this approach are demonstrated by model light scattering calculations for polypropylene matrix with different amount of spherical inclusions (voids, EPDM rubber particles, amorphous phase domains). The calculated turbidity values (based on the Lorenz-Mie (LM) theory^{11,12} and corrected for the multiple scattering effects) are compared with the results of the Debye-Bueche (DB) fluctuation theory for light scattering of optically heterogeneous materials¹³. Preliminary experimental results of relative absorbance for test specimens, with and without stress whitening, support the theoretical predictions.

THEORETICAL ASPECTS

There are several possibilities of evaluating and explaining optical properties of real polymer solids. Due to the extreme complexity of the solution of the radiation transfer theory¹⁴, the only feasible alternative is to make model computations based on assumed constituent properties. In this section, expressions are derived for parameters describing the scattering properties of a parallel-sided, smooth-surfaced slab of material containing randomly distributed spheres. In order to accommodate a wide range of practical situations, which may include materials containing spheres larger than the wavelength of light and having a significant refractive index mismatch with their surroundings, the exact LM theory is used to calculate the scattering properties of individual particles. Provided that the refractive index mismatch is small and the sphere diameter is comparable with the wavelength of incident light, a simplified approach may be used to predict the light scattering characteristics. The DB theory based on the fluctuation concept relates transmission properties to size and amplitude of refractive index fluctuation¹³. 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

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

where I_0 , I , ρ , τ , and l are the incident intensity, transmitted intensity, reflectivity, turbidity, and path length, respectively. Then, from the LM theory, the turbidity is given by¹² Eq. (2)

$$\tau = NC_{\text{sca}}(1 - \langle \cos \Theta \rangle_{\text{av}}) , \quad (2)$$

where N is number of spherical particles per unit volume having radius R , dispersed in a nonabsorbing medium and C_{sca} is scattering cross-section. The parameter $\langle \cos \Theta \rangle_{\text{av}}$ is the average value of the scattering vector used to include the effect of multiple scattering on the turbidity values. This parameter is called asymmetry factor. It is the mean of $\cos \Theta$ (Θ is the scattering angle) with the angular intensity as the weighting factor, i.e.¹⁵

$$\langle \cos \Theta \rangle_{\text{av}} = (\pi/k^2) \int_{-1}^{+1} (i_1 + i_2) \cos \Theta d(\cos \Theta)/C_{\text{sca}} , \quad (3)$$

where i_1 and i_2 are angular intensity functions¹⁵ corresponding to the components perpendicular and parallel, respectively, to the scattering plane (for the meaning of k , see Eq. (7)).

It is well known that the resonances in the Mie coefficients may cause oscillations of the scattering cross-sections for some sizes and relative refractive indices¹⁶. The sharp resonances need to be incorporated into the comparison of experiment with theory. To "smooth" the oscillations (an effect observable on the ideal sphere or spherical monodispersions only), the calculated values have been averaged over the diameter polydispersity of the sample that corresponded to the periodicity of resonances δx that is given¹⁶

$$\delta x = \arctan (n_r^2 - 1)^{-1/2} / (n_r - 1)^{1/2} , \quad (4)$$

where $\delta x = (2\pi/\lambda)\delta R$; R is sphere radius, λ is wavelength of light and n_r is the relative refractive index. Thus for any particular sphere it was assumed that there existed a spread of radii of total width of δx .

The second possible approach is based on the theoretical expression for the turbidity derived by Debye and Bueche¹³ and calculated using the correlation function

$$\Gamma(r) = \exp [-r/a] , \quad (5)$$

where a is the correlation length. The expression for the turbidity can be shown to be¹⁷

$$\tau = 32\pi^4(a^3/\lambda_0^4)\langle\eta^2\rangle\{[(b+2)^2/b^2(b+1)] - 2[(b+2)/b^3]\ln(b+1)\} , \quad (6)$$

where

$$b = 4k^2a^2, \quad k = 2\pi/\lambda \quad (7)$$

and the mean value of the refractive index fluctuations

$$\langle \eta^2 \rangle = \phi_1 \phi_2 (n_1 - n_2)^2, \quad (8)$$

where $\phi_1 \phi_2$ are volume fractions and n_1, n_2 refractive indices of both phases. For calculation of scattering cross-sections, asymmetry factors and corresponding turbidities we used the Mie3 program^{18,19} (implementation of the LM theory) and Eq. (2).

The model calculations were carried out for three systems: (i) matrix of isotactic polypropylene containing voids, (ii) polypropylene containing particles of ethylene-propylene (EPDM) rubber and (iii) matrix of isotactic polypropylene containing spherical inclusions with refractive index corresponding to that of amorphous phase. We included into the calculation of turbidity both the effects of refractive index dispersion (the dependence of refractive index on the wavelength) and the change of refractive index of the matrix medium due to the presence of the minor phase. The former effect has been taken into account using the empirical relationship developed by Cauchy in the form¹⁷

$$n(\lambda) = A + B/\lambda^2. \quad (9)$$

The constants in Eq. (9) for both materials have been determined experimentally by using refractometer and selected spectral lines emitted by the Hg lamp and a line of a He-Ne laser. The concentration dependence of refractive index of the medium n_m has the simple form of the mixing rule

$$n_m = n_1 + V(n_2 - n_1), \quad (10)$$

where V is the volume fraction of the minor phase.

MODEL CALCULATIONS AND EXPERIMENTS

In all three considered systems monodisperse spherical particles or voids were assumed (with the diameter spread eliminating the resonance effects, cf. Eq. (4)). In Fig. 1 we

compare the values of turbidities calculated by means of Eqs (2) and (6) in the range of small inclusions of EPDM in the PP matrix. It can be seen that for $d/\lambda < 0.3$ there exists a good accord between the LM and DB theory as discussed in more detail elsewhere²⁰.

The following diameters of scattering spheres were put into the calculations of turbidities for the larger inclusions, where the use of the LM theory (Eq. (2)) is necessary: from 0.1 to 1.0 μm with a step of 0.1 μm or from 1 to 10 μm with a step of 1 μm for

TABLE I
Relevant refractive indices: spectral and compositional dependence

Wavelength μm	Refractive indices	
	polypropylene	polypropylene matrix
		$V = 0.1$ $V = 0.3$
0.4	1.5252	1.4870 1.4952
1.0	1.5058	1.4700 1.4780
	EPDM	polypropylene matrix
		$V = 0.1$ $V = 0.3$
0.4	1.4873	1.5149 1.5088
1.0	1.4813	1.5008 1.4965
	voids	polypropylene matrix
		$V = 0.1$ $V = 0.3$
0.4	1.0	1.47268 1.36764
1.0	1.0	1.45522 1.35406

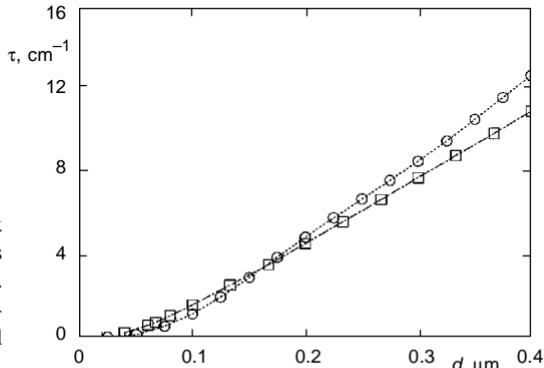


FIG. 1
Size effect of EPDM inclusions in PP matrix on turbidity. Volume fraction of inclusions is 0.1, the wavelength of light is 0.6 μm . The results of the LM (○) and DB (□) theories are in relatively good accord for small inclusions ($d/\lambda < 0.3$)

voids or rubber particles in PP matrix, respectively. The selected spectral range was 0.4–1.0 μm and volume fractions of minor phase were 0.1 and 0.3. The overview of relevant refractive indices is given in Table I. It appears instructive to compare the optical characteristics of the polypropylene samples containing voids with the same material filled with EPDM rubber. The comparison is presented in Figs 2 and 3 for the diameter range from 0.1 to 5 μm , two volume concentrations (0.1 and 0.3) and wavelengths $\lambda = 0.4 \mu\text{m}$ and 1.0 μm . Figure 4 illustrates the turbidities of the semicrystalline

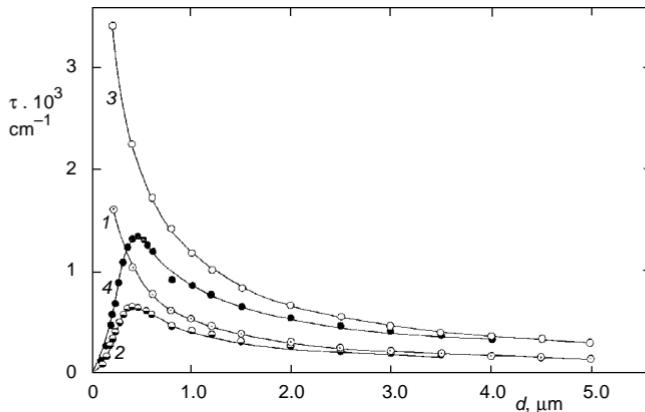


FIG. 2

Voids in polypropylene: Size and concentration effects on turbidity at two wavelengths $\lambda = 0.4$ and 1.0 μm . Volume fraction $V = 0.1$: $\lambda = 0.4 \mu\text{m}$ (1), $\lambda = 1.0 \mu\text{m}$ (2); $V = 0.3$: $\lambda = 0.4 \mu\text{m}$ (3), $\lambda = 1.0 \mu\text{m}$ (4)

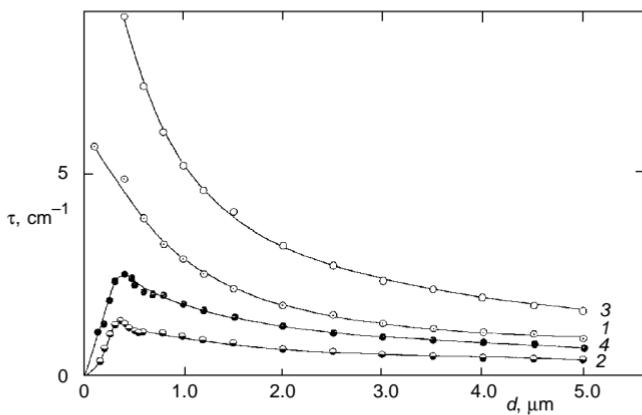


FIG. 3

Ethylene-propylene rubber particles in polypropylene: Size and concentrations effects on turbidity at two wavelengths $\lambda = 0.4$ and 1.0 μm . Volume fraction $V = 0.1$: $\lambda = 0.4 \mu\text{m}$ (1), $\lambda = 1.0 \mu\text{m}$ (2); $V = 0.3$: $\lambda = 0.4 \mu\text{m}$ (3), $\lambda = 1.0 \mu\text{m}$ (4)

polypropylene samples filled with given volume fractions of crystalline phase under identical conditions. In Figs 2–4 two characteristic features can be observed: *First*, all samples display turbidity maxima at wavelength $\lambda = 1.0 \mu\text{m}$ corresponding to the diameter of the scattering particles about $0.4 \mu\text{m}$; samples with rubber particles show separated spectral and concentrations effects, whereas for voids these effects overlap.

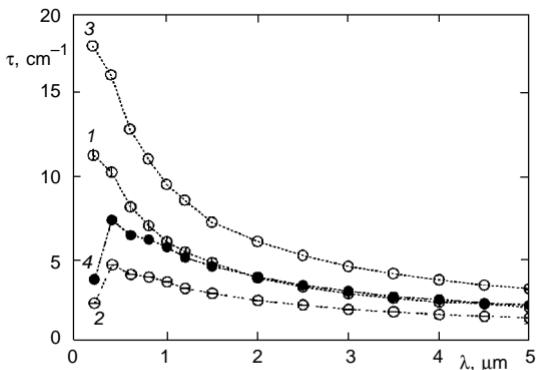


FIG. 4

Spherical inclusions of crystalline phase in the matrix of isotactic polypropylene: Size and concentration effects on the turbidity at two wavelengths $\lambda = 0.4$ and $1.0 \mu\text{m}$. Volume fraction $V = 0.1$: $\lambda = 0.4 \mu\text{m}$ (1), $\lambda = 1.0 \mu\text{m}$ (2); $V = 0.3$: $\lambda = 0.4 \mu\text{m}$ (3), $\lambda = 1.0 \mu\text{m}$ (4)

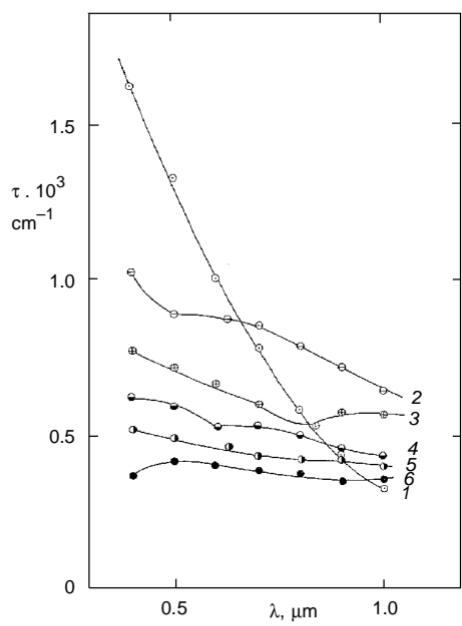


FIG. 5

Spectral dependence of turbidity for voids (volume fraction 0.1) in polypropylene: Void diameter $d = 0.2 \mu\text{m}$ (1), $0.4 \mu\text{m}$ (2), $0.6 \mu\text{m}$ (3), $0.8 \mu\text{m}$ (4), $1.0 \mu\text{m}$ (5) and $1.2 \mu\text{m}$ (6)

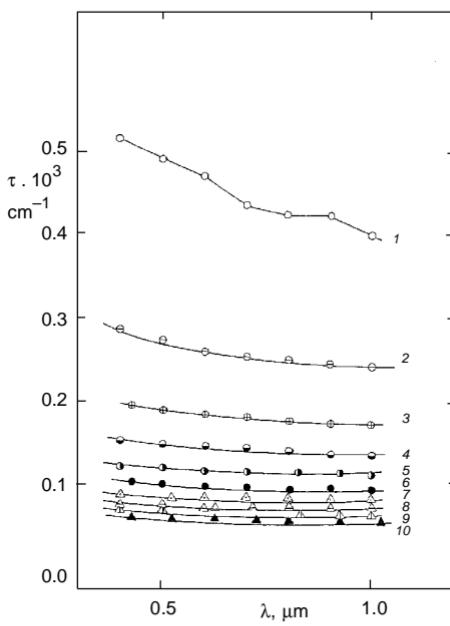


FIG. 6

Spectral dependence of turbidity for voids (volume fraction 0.1) in polypropylene: Void diameter $d = 1 \mu\text{m}$ (1), $2 \mu\text{m}$ (2), $3 \mu\text{m}$ (3), $4 \mu\text{m}$ (4), $5 \mu\text{m}$ (5), $6 \mu\text{m}$ (6), $7 \mu\text{m}$ (7), $8 \mu\text{m}$ (8), $9 \mu\text{m}$ (9) and $10 \mu\text{m}$ (10)

The samples with crystalline spherical inclusions occupy the intermediate position. *Second*, in every case the turbidity values are about two orders of magnitude larger for polypropylene with internal voids than those for polypropylene with EPDM particles or spherical inclusions of the crystalline phase (note the different scales on vertical axis). In Figs 5–8, spectral dependences of turbidity are summarized for the same systems, but with a lower volume filling, 0.10. Specifically, Fig. 5 gives results for voids of diameter from 0.2 to 1.2 μm and Fig. 6 covers the void diameter range from 1 to 10 μm . Analogous data of calculated spectral dependences of turbidity for polypropylene con-

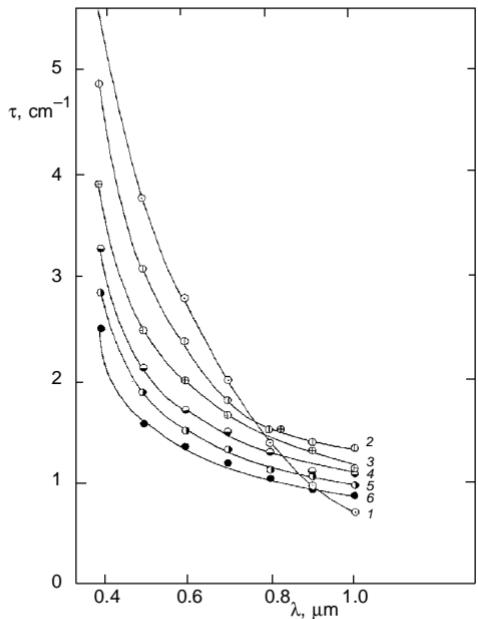


FIG. 7

Spectral dependence of turbidity for ethylene-propylene rubber particles (volume fraction 0.1) in polypropylene: Particle diameter $d = 0.2 \mu\text{m}$ (1), $0.4 \mu\text{m}$ (2), $0.6 \mu\text{m}$ (3), $0.8 \mu\text{m}$ (4), $1.0 \mu\text{m}$ (5) and $1.2 \mu\text{m}$ (6)

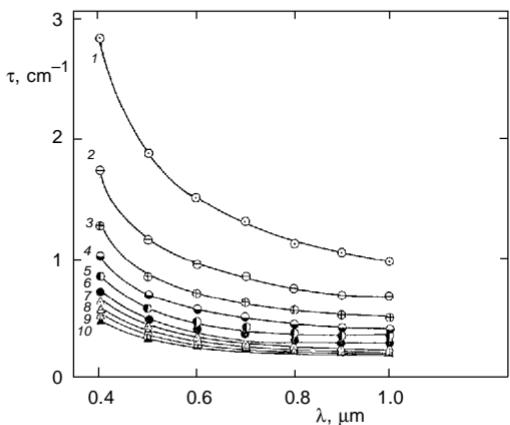


FIG. 8

Spectral dependence of turbidity for ethylene-propylene rubber particles (volume fraction 0.1) in polypropylene: Particle diameter $d = 1.0 \mu\text{m}$ (1), $2 \mu\text{m}$ (2), $3 \mu\text{m}$ (3), $4 \mu\text{m}$ (4), $5 \mu\text{m}$ (5), $6 \mu\text{m}$ (6), $7 \mu\text{m}$ (7), $8 \mu\text{m}$ (8), $9 \mu\text{m}$ (9) and $10 \mu\text{m}$ (10)

taining EPDM rubber are given in Figs 7 and 8. The comparison immediately reveals a principal difference in optical behaviour of both systems. While spectral dependence of turbidity is slight in Figs 5 and 6 (corresponding to polypropylene with voids), a much steeper spectral dependence of turbidity can be seen in Figs 7 and 8. This fact is illustrated in Table II, where the ratio of turbidities at two wavelengths ($\lambda = 0.4 \mu\text{m}$ and $\lambda = 1.0 \mu\text{m}$) are compared for different particle sizes and two concentrations for all three systems with optical parameters summarized in Table I.

The difference between the absolute values of the turbidities for samples with voids and those with EPDM particles is at least two orders of magnitude. Similar results obtained for PP samples with different amount of crystalline phase are not surprising as the refractive index of EPDM particles corresponds roughly to that of polypropylene

TABLE II

Turbidity ratios^a $\tau_{0.4}/\tau_{1.0}$ for polypropylene matrix with propylene inclusions, EPDM particles or voids: size and concentration effects

Diameter d μm	Volume fraction V_i					
	PP-PP inclusions		PP-EPDM		PP-voids	
	0.1	0.3	0.1	0.3	0.1	0.3
0.2	4.68	4.73	7.92	7.98	5.02	5.97
0.4	2.19	2.22	6.50	3.65	1.59	1.72
0.6	1.99	2.02	3.45	3.47	1.38	1.45
0.8	1.78	1.81	2.98	3.01	1.43	1.51
1.0	1.67	1.69	2.88	2.88	1.30	1.35
1.2	1.66	1.70	2.82	2.83	1.25	1.30
2	1.54	1.56	2.60	2.60	1.18	1.22
3	1.49	1.51	2.51	2.50	1.14	1.17
4	1.47	1.49	2.45	2.48	1.12	1.14
5	1.46	1.48	2.38	2.41	1.09	1.12
6	1.45	1.47	2.34	2.38	1.09	1.11
7	1.45	1.46	2.34	2.36	1.07	1.09
8	1.45	1.46	2.31	2.12	1.08	1.04
9	1.44	1.46	2.28	2.32	1.07	1.09
10	1.44	1.46	2.28	2.30	1.07	1.08

^a At wavelengths 0.4 and 1.0 μm .

amorphous phase. It can be inferred from Table I that the turbidity ratio is remarkably independent of the concentration of the minor phase (voids, EPDM particles or spherical inclusions with slightly different refractive indices) and is for larger diameters (above ca 1 μm) only slightly dependent on the size of the minor phase structures. In any case the ratio $\tau(0.4)/\tau(1.0)$ for voids displays a very mild dependence in comparison with both PP-EPDM and PP-amorphous inclusions systems.

In this work main interest has been devoted to the turbidities, i.e. to the transmission properties of heterogeneous polymeric systems. However, for deeper understanding of

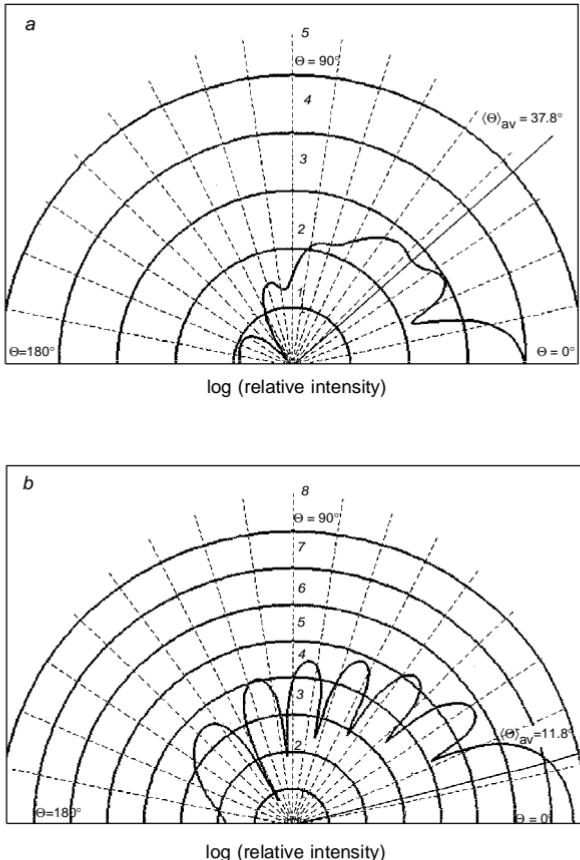


FIG. 9
 Calculated scattered light intensity as a function of the scattering angle for vertically polarized plane wave (the levels of the same intensity are denoted by numbers); *a* voids in polypropylene, *b* EPDM particles in polypropylene. Diameter of scatterers $d = 1 \mu\text{m}$, their volume fraction $V = 0.1$, wavelength $\lambda = 0.4 \mu\text{m}$. The angle $\langle \Theta \rangle_{av}$ corresponding to the asymmetry factor $\cos \langle \Theta \rangle_{av}$ (cf. Eq. (3)) is indicated by the solid line. Note the relative intensity units on the horizontal axis. The ratio of absolute scattering intensities for $\Theta = 0$ in *a* and *b* is approximately 76 : 1

the turbidity differences between specimens with voids and particles, a comparison of complete angular dependences of the scattered light intensity can be useful. An example for scatterers of diameter $d = 1 \mu\text{m}$ and wavelength $\lambda = 0.4 \mu\text{m}$ is presented in Figs 9a and 9b. Three distinct differences should be indicated: *First*, the shape of the indicatrix is markedly different for voids and particles. *Second*, a marked difference in asymmetry factors influencing the turbidity data (Eq. (3)) is demonstrated. *Third*, the ratio of transmitted intensities for $\Theta = 0$ between voids and particles is 76 : 1. (The latter, however, cannot be directly read out from Fig. 9 as the plots are given in relative units). It should be also noted that two effects exist in real polymer samples that could complicate the results given above, namely the effects of particle size distribution and nonspherical scatterers. The calculated scattering cross-sections have been averaged over the diameter δx to smooth the oscillations caused by the resonance effects, so that the studied system is not strictly monodisperse. Recent studies have shown that the polydispersity effect is manageable in the Rayleigh–Gans–Debye approximation only²¹. The effect of particle anisometry is usually solved by means of an assumption of spheroidal shape, where a root-mean-square radius of a spheroid can be expressed as $r = [(2a^2 + c^2)/3]^{1/2}$. The geometry of the spheroid is derived from characteristic dimensions a, a, c of an anisometric rotational ellipsoid, with c measured in the direction of the rotational symmetry axis. From calculations for spherical and ellipsoidal particles it appears that such approximation of anisometric scatterer by an equivalent spherical particle is quite reasonable.

The preliminary experimental results supporting the predicted spectral behaviour of turbidity for typical specimens are given in Fig. 10, where we compared the experimental results of relative absorbance (proportional to the turbidity) obtained with a Perkin–Elmer 340 spectrophotometer by using the integrating sphere accessory. The samples used were standard dumb-bell test specimens (thickness about 3 mm). As predicted in Table II, the stress-whitened sample has only mild spectral dependence as compared

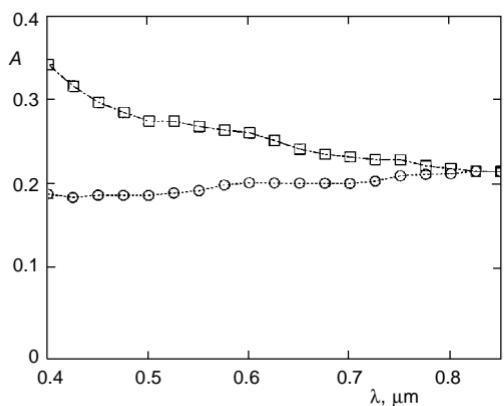


FIG. 10
Experimental spectral dependences of relative absorbance A (proportional to the turbidity) for two polypropylene specimens: 1 non-deformed injection molded polypropylene (decreasing dependence is typical of light scattering by embedded particles); 2 the same specimen after solid-state drawing at 100 °C (flat dependence reveals voids as light scatterers)

with the semicrystalline undeformed test specimen. The experimental data are not corrected for the sample thickness, so that the relative absorbance is comparable for both specimens.

The results of the presented calculations can be summarized as follows:

a) In spite of its relative simplicity the fluctuation theory of Debye and Bueche (Eqs (5)–(8)) gives turbidity values in good accord with the predictions of the concept of Lorenz and Mie (Eqs (1)–(3)), when the effects of dispersion and concentration are included (cf. Fig. 1) and when the ratio of particle diameter to the wavelength d/λ is < 0.3 . For larger particles, however, the use of the LM theory is necessary²⁰.

b) The magnitude of turbidity for voids in polypropylene matrix is at least hundred times larger as compared with the system of EPDM rubber particles in polypropylene at the same concentrations, wavelength and thicknesses.

c) The turbidity ratios at two different wavelengths are markedly larger for polypropylene with rubber particles or polypropylene with inclusions of crystalline phase as compared to those with voids (see Table I). The theoretical difference offers a possibility of assessing the origin of stress-whitening in real polymer materials. Preliminary experimental results support the predicted spectral dependence of turbidity for well defined specimens (see Fig. 10).

d) The effect of concentration (increasing volume fractions) of the light scatterers on the absolute turbidity value is more pronounced for voids as compared with rubber particles. In the case of very small voids (about $0.2 \mu\text{m}$), the concentration effect even overshadows the spectral dependence. Therefore, the size polydispersity of particles could complicate the calculations only with very small particles.

e) The application of the above approach to other polymer systems with known optical parameters is straightforward²². Extended experimental application of the described turbidity method to real polymer systems containing both voids and particles is the subject of our further study.

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REFERENCES

1. Kambour K. H.: *J. Polym. Sci., Macromol. Rev.* **7**, 1 (1973).
2. Jareki L., Meier D. J.: *J. Polym. Sci., Polym. Phys. Ed.* **17**, 1611 (1979).
3. Wendorf J. H.: *Prog. Coll. Polym. Sci.* **67**, 165 (1980).
4. Connor K. M. O., Wool R. P.: *J. Appl. Phys.* **51**, 75 (1980).
5. Oh B. S., Kim H. S., Ma P.: *Polym. Mater., Sci. Eng.* **71**, 11 (1994).
6. Breuer H., Haaf F., Stabenow J.: *J. Macromol. Sci., Phys.* **14**, 387 (1977).
7. Smith J. W., Kaiser T.: *J. Mater. Sci.* **23**, 3833 (1988).
8. Jenke D. R.: *J. Appl. Polym. Sci.* **44**, 1223 (1992).
9. Lee Y. W., Kung S. H.: *J. Appl. Polym. Sci.* **46**, 9 (1992).

10. Rengarajan R., Kesavan S. K., Fullerton K. L., Lee S.: *J. Appl. Polym. Sci.* **45**, 317 (1992).
11. van de Hulst H. C.: *Light Scattering by Small Particles*. Wiley, New York 1957.
12. Gate L. F.: *J. Opt. Soc. Am.* **63**, 312 (1972).
13. Debye P., Bueche A. M.: *J. Appl. Phys.* **20**, 518 (1949).
14. van de Hulst H. C.: *Multiple Light Scattering, Tables, Formulas and Applications*, Vol. 1 and 2. Academic Press, New York 1980.
15. Kerker M.: *The Scattering of Light*. Academic Press, New York 1969.
16. Chylek P., Kiehl J. T., Ko M. K. W: *J. Colloid Interface Sci.* **64**, 595 (1978).
17. Meeten G. H. (Ed.): *Optical Properties of Polymers*. Elsevier, London 1986.
18. Gouesbet G., Grehan G., Maheu B.: *Appl. Opt.* **22**, 2038 (1983).
19. Corbin F., Grehan G., Gousbet G., Maheu B.: *J. Part. Syst. Charact.* **5**, 103 (1988).
20. Holoubek J.: *Collect. Czech. Chem. Commun.* **58**, 2272 (1993).
21. Penders M. H. G. M., Vrij A.: *J. Chem. Phys.* **93**, 3704 (1990).
22. Holoubek J., Han Ch. C.: *Polym. Mater., Sci. Eng.* **71**, 368 (1994).