

## Light scattering by optically heterogeneous polymer systems: stress whitening in polypropylene materials

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### Summary

A theoretical background is presented which allows the assessment of the physical nature of turbidity in heterogeneous polymeric materials. The theory (based on the diffusion approximation of the transfer theory and Kubelka-Munk theory) predicts a decreasing spectral dependence of turbidity with increasing wavelength for a matrix with embedded particles of slightly different refractive indices, but a flat dependence of this quantity for a matrix material with microvoids. It is demonstrated that the diffuse reflectance displays the same type of wavelength dependence for the thick layer approximation. Indeed, diffuse light reflectance experiments on bulk specimens using an integrating sphere accessory reveal the first type of behaviour for nondeformed neat and rubber-modified polypropylenes. On the other hand, the second type of behaviour was observed with stress-whitened neat and rubber-modified polypropylenes after solid-state drawing.

### Introduction

Light scattering is a powerful tool to study polymer morphology (1,2). Unlike microscopical information, which could be biased by a subjective approach, light scattering yields average integral data and allows to characterize a polymer in bulk both in the solid state and in the melt. From the scattering point of view, polymer systems of industrial interest typically do not satisfy the single scattering regime and produce multiple scattering with even relatively thin samples (1). Several approaches to calculating the light scattering and propagation in a given situation from the basic properties can be found (3,4). In this paper diffusion approximation of the transport theory is used (1,4,5), which is valid if the absorption cross-section  $C_a$  is small compared with the scattering cross-section  $C_{sca}$ .

The origin of turbidity and stress whitening in semicrystalline polymers and blends are still a matter of some controversy (6-9). We studied the transmission and reflectance properties of the stress-whitened specimens of semicrystalline polypropylene (PP), with or without embedded particles (various fractions of amorphous phase, ethylene-propylene rubber particles (EPDM) or open voids), by model computations, measurements of relative diffuse reflectance in visible region and by immersion experiment which showed a long-term transparence recovery of the stress-whitened specimen. It has been shown that the ratio of turbidities and reflectances at two wavelengths from the opposite parts of the visible spectra depends only slightly on the particle concentration (5,10,11). Such dependences calculated for PP containing voids on the one hand or particles, differing only slightly from the surrounding matrix in their refractive index on the other (EPDM particles or spherical inclusions of crystalline and/or amorphous phase in PP matrix) are markedly different (11). Thus, the nature of stress whitening in complex polymeric materials

can be determined from turbidity or reflectance measurements. Model calculations fit the experimental curves of relative diffuse reflectance  $R$  very well and a direct support of the existence of connected voids is presented based on the restoration of the original transparency of the stress-whitened specimen in an immersion liquid.

### Theoretical

The validity of the diffusion approximation is restricted to cases in which the reduced albedo  $a(1, 3-5, 11, 12)$  is close to unity

$$a = C'_{sca} / (C_a + C'_{sca}) \cong 1 \quad (1)$$

where  $C_a$ ,  $C_{sca}$  and  $C'_{sca}$  are absorption, scattering and reduced scattering cross-sections, respectively. The last quantity is defined by means of the asymmetry factor  $g$  as

$$C'_{sca} = C_{sca} (1 - g) \quad (2)$$

The parameter  $g$  is the mean value of  $\cos \theta$  ( $\theta$  being the scattering angle) with the angular intensity as the weighting factor (4,5,12,13). Hence,

$$g = (\pi / k) \int_{-1}^1 (i_1 + i_2) \cos \theta / C_{sca} d(\cos \theta) \quad (3)$$

where  $k = 2\pi / \lambda$ . If the intensity functions  $i_1$  and  $i_2$  are of the Lorenz-Mie type (1,3,12), the asymmetry factor  $g$  can be calculated from the classic scattering coefficients  $a_n$  and  $b_n$ . The transmittance law for this regime (the Beer-Lambert law) must be modified by the inclusion of the reduced scattering cross-sections. For the turbidity  $\tau$  we then have

$$\tau = NC'_{sca} = NC_{sca} (1 - g) \quad (4)$$

where  $N$  is number of spherical particles per unit volume having radius  $r$ . In the thick-layer approximation, when collimated transmitted flux is very small, we obtain for a diffuse reflectance  $R(1)$

$$R = SZ (1 + SZ) \quad (5)$$

where  $S$  is scattering parameter from the Kubelka-Munk theory (1,3) and  $Z$  is layer thickness. The  $S$  parameter is then

$$S = (3/4) NC_{sca} (1 - g) \quad (6)$$

For the ratio of diffuse reflectances at two different wavelengths we get relation

$$R(\lambda_1) / R(\lambda_2) = S(\lambda_1) [1 + S(\lambda_2) Z] / S(\lambda_2) [1 + S(\lambda_1) Z] \quad (7)$$

Nowadays several software packages exist (14-16) enabling computations of  $C_{sca}$  and  $g$  and thus determination of  $S$  and  $R(\lambda_1) / R(\lambda_2)$ . We used the Mie3 program (17,18) (implementation of the Lorenz-Mie theory) and Eq.(2) in our calculation of scattering cross-sections, as well as asymmetry factors and corresponding quantities in Eq.(4) and (5).

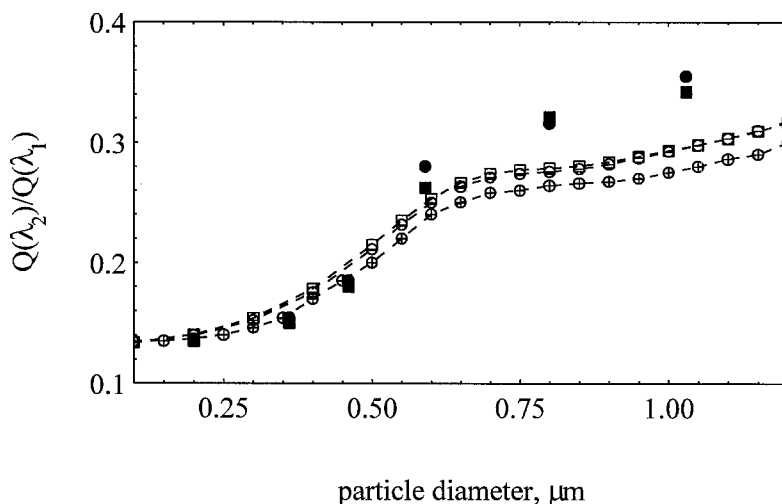
It is well known that the resonances in the Mie coefficients may cause oscillations of the scattering cross-sections for some sizes and relative refractive indices (19). To "smooth" the oscillations (an effect observable on the ideal sphere or spherical mono-dispersions only), the calculated values have been averaged over the diameter-poly-

dispersity of the sample that corresponded to the periodicity of resonances  $\delta x$ . Thus for any particular sphere it was assumed that there existed a spread of total width of  $\delta x$  (11).

Model calculations were carried out for three systems: (a) matrix of isotactic polypropylene containing voids, (b) polypropylene containing particles of ethylene-propylene (EPDM) rubber and (c) matrix of isotactic polypropylene containing spherical inclusions with refractive indices corresponding to those of amorphous and crystalline phases, respectively. 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 in refractive index of the matrix medium due to the presence of the minor phase (11,12).

### Model calculations and experiments

A reasonable agreement has been found between the experimental and calculated values of the scattering cross-section for various polymer systems up to a volume fraction of 0.2 under the diffusion approximation (20). There are few published experimental data for light scattering from high volume fractions of scattering particles that have diameters larger than the wavelength used for illumination. In Figure 1 we illustrated the experimental data from literature (10) together with theoretical results obtained with the described procedure. The accord is very good for diameters smaller than cca 0.6  $\mu\text{m}$ , for larger diameters the difference could be ascribed to the low transmission of larger polystyrene particles in water in the near infrared region, where the use of the diffraction approximation (eq.(1)) can be questionable, and to the uncertainty in refractive indices extrapolated from the visible region. A recent study of scattering from large particles (21) includes a limited range of relative refractive indices only and cannot be used for



**Figure 1.** Comparison of calculated and measured scattering efficiency  $Q_{\text{sca}} = C_{\text{sca}} / \pi r^2$  of polystyrene microspheres suspended in water. ( $r$  is microsphere radius,  $\lambda_1 = 1.13 \mu\text{m}$ ,  $\lambda_2 = 2.29 \mu\text{m}$ ).

( $\oplus$ ) theoretical data: without dispersion correction of refractive indices (ref. 10);  
 ( $\circ$ ), ( $\square$ ) theoretical data with the corrections; ( $\bullet$ ), ( $\blacksquare$ ) experimental data from ref. 10.  
 Volume fractions ( $\circ$ ), ( $\blacksquare$ ) 0.02 ( $\square$ ), ( $\bullet$ ) 0.05

comparison. In all three solid systems considered hereinafter, monodisperse spherical particles (12) or voids were assumed (with the diameter spread eliminating the resonance effects). An overview of relevant refractive indices for voids, rubber particles and PP inclusions in PP matrix, are given in Table 1. We introduce only spectral dependences  $\tau(0.4)/\tau(0.8)$ , i.e. the ratios of turbidities at  $\lambda=0.4$  and  $0.8 \mu\text{m}$  and volume fractions of minor phase, 0.1 and 0.3, that can be compared with experimental data. The calculations indicated that the spectral dependence of turbidity is weak for voids in PP matrix (horizontal plateau of  $\tau(0.4)/\tau(0.8)$  close to unity demonstrates a negligible spectral dependence of turbidity). A much steeper spectral dependence of turbidity can be expected for all types of inclusions as seen in Figure 2, where the turbidity ratios at two wavelengths are compared for different particle sizes and two concentrations for all three systems with optical parameters given in Table 1. It can be inferred from Figure 2 that the turbidity ratio is virtually insensitive to the concentration of the minor phase. The data points calculated for two different volume fractions (0.1 and 0.3) of the minor phase are located on the same curves. However, the curves distinctly differ for voids, EPDM particles or inclusions with refractive index slightly different from PP matrix, respectively. The  $\tau(0.4)/\tau(0.8)$  ratio for larger inclusions (diameters larger than cca  $1 \mu\text{m}$ ) depends on the inclusion size but slightly.

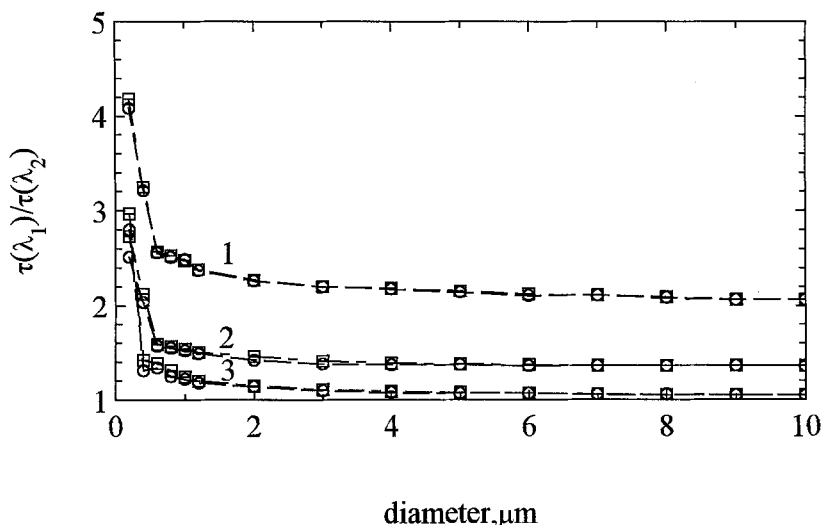
Table 1. Relevant refractive indices for studied systems:  
spectral and compositional dependence

Wavelength [ $\mu\text{m}$ ]	Refractive Indices		
	polypropylene (amorphous)	polypropylene matrix V=0.1      V=0.3	
0.4	1.4832	1.5021	1.4952
0.8	1.4632	1.4859	1.4795
	EPDM	polypropylene matrix V=0.1      V=0.3	
0.4	1.4873	1.5025	1.4991
0.8	1.4820	1.4873	1.4879
	voids	polypropylene matrix V=0.1      V=0.3	
0.4	1.0	1.4538	1.4391
0.8	1.0	1.4391	1.3415

The ratio  $\tau(0.4)/\tau(0.8)$  for voids displays a very mild dependence in comparison with both PP + EPDM and PP + amorphous inclusions. Due to practical independence of turbidity ratios on the particle diameters (cf. Fig. 2), the size polydispersity effects do not play any significant role for diameters larger than ca  $1 \mu\text{m}$ .

The effect of particle anisometry caused by stress is usually dealt with by means of an assumption of spheroidal shape (with dimensions a,a,c), where a root-mean-square

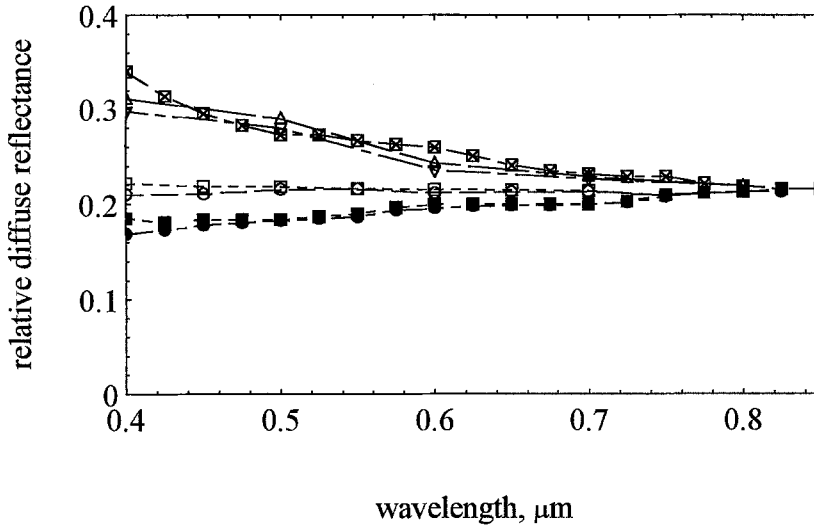
radius of a spheroid can be expressed as  $r = [(2a^2 + c^2)/3]^{1/2}$ . From calculations for spherical and ellipsoidal particles it appears that such approximation of anisometric scatterer by an equivalent spherical particle is quite reasonable (22).



**Figure 2.** Comparison of turbidity ratio  $\tau(\lambda_1)/\tau(\lambda_2)$  for various polypropylenes ( $\lambda_1 = 0.4 \mu\text{m}$ ,  $\lambda_2 = 0.8 \mu\text{m}$ ); 1 PP with EPDM rubber, 2 PP with spherical inclusions of amorphous phase, 3 PP with spherical voids  
Volume fraction (O), 0.1, (□) 0.3

### Results and Discussion

We measured the relative diffuse reflectance (proportional to the turbidity, cf. eqs. (2-5)) with a Perkin-Elmer 340 spectro-photometer using an integrating sphere accessory in the spectral region 0.4–0.85  $\mu\text{m}$ . The samples used were standard dumb-bell test specimens with optical parameters given in Table 1. The experimental results for typical specimens are given in Figure 3. We used neat polypropylene Mosten 58412 (Chemopetrol, Czech Republic), cross-section  $10 \times 4 \text{ mm}$  (thickness) and a specimen of the same polymer deformed at drawing temperature  $T_d = 100^\circ\text{C}$ . The reactive type of rubber-modified polypropylene Kelburon KLB 9569X (DSM Holland) was deformed at  $T_d = 23^\circ\text{C}$ . As predicted in Figure 2, the stress-whitened samples (both with voids and voids plus EPDM inclusions) show only mild spectral dependences as compared with the semicrystalline undeformed test specimen. Hence, a flat spectral dependence indicates voids as light scatterers, whereas a decreasing spectral dependence is typical of light scattering by embedded particles. The experimental data are normalized at  $\lambda = 0.85 \mu\text{m}$  by shifting curves to cross in this point to allow comparison of all samples in the same figure. The experimentally observed increasing  $R(\lambda)$  dependence cannot be obtained from the  $\tau(\lambda)$  theoretical dependences for any reasonable particle diameters (1–80  $\mu\text{m}$ ), whereas the  $C_{\text{scat}}(0.4)/C_{\text{scat}}(0.8)$  can be smaller than unity for very large particles (diameters in tens of microns). This might indicate the role of collimated flux and needs a further detailed study.



**Figure 3.** Comparison of calculated and experimental relative diffuse reflectances for various polypropylenes

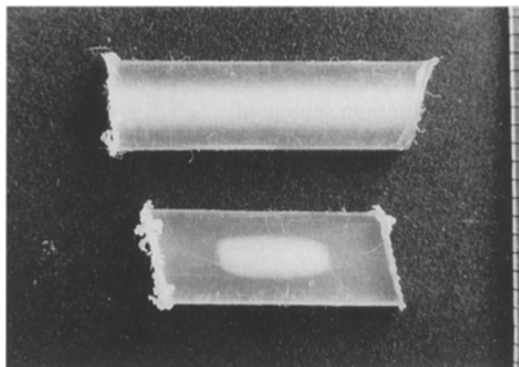
( $\boxtimes$ ) non-deformed injection-molded PP (experimental); ( $\blacksquare$ ) deformed injection-molded PP after solid-state drawing at 100 °C (experimental); ( $\bullet$ ) PP with EPDM microspheres after solid state drawing at 100 °C (experimental).

PP with spherical voids ( $\square$ )  $R = 4 \mu\text{m}$ , ( $\circ$ )  $R = 15 \mu\text{m}$  (calculated); PP with spherical inclusions of amorphous phase ( $\nabla$ )  $R = 4 \mu\text{m}$  (calculated); PP with spherical inclusions of EPDM ( $\Delta$ )  $R = 4 \mu\text{m}$  (calculated). All curves are shifted to cross at  $\lambda = 0.85 \mu\text{m}$ . Volume fraction of minor phase is 0.1.

A direct proof of interconnected voids in the studied stress-whitened samples can be obtained by immersion of the sample into a suitable solvent (23). We selected n-heptane, known as preferential solvent of polypropylene amorphous phase (24). Figure 4 shows the original stress-whitened sample together with the same sample after 2 weeks immersion in n-heptane at room temperature. The almost total transparency recovery is seen at both sides of the broken sample, where the solvent uptake is supported by the connected open voids system.

The results can be summarized as follows:

- The turbidity ratios and diffuse reflectance values 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. The difference offers a possibility of diagnosing the origin of stress-whitening in real polymeric materials.
- Experimental results (relative diffuse reflectance) support the predicted spectral dependence of turbidity for all three systems under consideration.
- Direct measurements of transparency recovery in a stress-whitened specimen in an immersion liquid confirmed the existence of a connected void system



**Figure 4.** Partial recovery of transparency of drawn polypropylene after immersion in n-heptan. Original stress whitened sample after solid state drawing at 100°C (top); (bottom) recovery of transparency from both sides due to permeation of solvent into the connected void system. Size marks on the right are 1 mm.

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