Light Scattering and Reflectance of Optically Heterogeneous Oriented Polymers

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Summary: A simple approach is used to measure the reduced scattering coefficient μ'_s of a thick turbid medium having a small absorption coefficient $\mu'_a << \mu'_s$. Based on the light reflectance measurement of semi-infinite media with a CCD camera, the shift between the centre of the incident laser beam and the centre of the diffuse background, Δx, is determined which is inversely proportional to μ'_s. The experimental values of μ'_s determined for (i) EPDM particles in a polypropylene matrix and (ii) the specific case of oriented PMMA domains in a polycarbonate matrix are compared with model calculations using the Lorenz-Mie theory and a simple approximation of light scattering theory by spheroidal particles. A comparison of theoretical data with parameters from image analysis of SEM pictures gives a good accord. The dependence of light scattering patterns on mutual orientation of incident light beam and of spheroidal particles is discussed.

Introduction

Most polymer blends and composites form a multiphase system with a deformable minor phase; under appropriate conditions, morphological structures such as spheres, ellipsoids, fibres, and plates may be produced[1]. As a result, development of rapid on- and off-line techniques to measure the size, shape and volume fraction of the minor phase is important. Optical methods are attractive for the on-line characterization of polymer materials but a limitation of conventional light scattering techniques is their requirement for relatively thin samples so that multiple scattering effects may be avoided[2-4]. The approach described in this paper is proposed to circumvent this limitation.

Recently[5], a hybrid model of the Monte Carlo (MC) simulation and diffusion theory has been described, which combines the accuracy of MC simulation and the speed of diffusion theory. As a result, not only thick samples but even a semi-infinite material with access to its single side may be inspected. The value of reduced scattering coefficient determined from experiment is an important structural parameter with direct relationship to size of particles and their volume fraction in the polymer matrix. The application of the above mentioned

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method to PP samples with various amounts of ethylene-propylene rubber particles (EPDM) has been recently presented[6].

A more complicated case of light scattering by oriented particles is discussed for anisometric domains of PMMA in the PC matrix. Complete solution of the light scattering problem for such a system is very complex and hence even approximate solution is desirable and instructive.

Theory

Optical properties of a semi-infinite turbid medium can be described using four parameters: relative refractive index n_r, absorption coefficient μ_a, scattering coefficient μ_s, and anisotropy factor[7] g. The relative refractive index n_r is the ratio between the refractive indices of the turbid and ambient medium. The absorption coefficient μ_a is defined as the probability of photon absorption per unit infinitesimal path-length, and the scattering coefficient μ_s is defined as the probability of photon scattering per unit infinitesimal path-length. The anisotropy factor g is the average cosine of the scattered angle, where the scattering of material is well represented by the Lorenz-Mie scattering functions[7-9].

For a semi-infinite medium whose $\mu_a << \mu_s$, a simple and rapid approach to measurement of the reduced scattering coefficient, $\mu'_s = \mu_s (1 - g)$, has been derived[5]. A laser beam with an oblique angle of incidence to the medium, α_i, causes the centre of the diffuse reflectance, which is several transport mean-free paths away from the incident point, to shift away from the point of incidence by a length Δx (cf. Fig. 1). This amount is used to compute μ'_s by

$$\mu'_s = \sin \alpha_i/(n_r \Delta x) \qquad (1)$$

The following subsections describe experimental testing of Eq. (1), a comparison with computations of the reduced scattering coefficient in the diffusion approximation using the Lorenz-Mie theory, the asymmetry factor and an effective refractive index of the medium

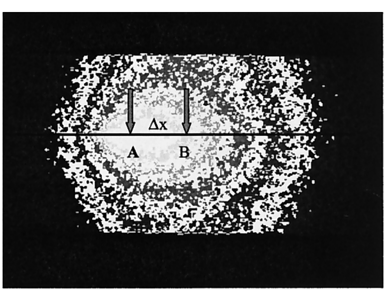

Fig. 1: A diffuse reflectance pattern from sample PPR1 (Table 1) obtained with a CCD camera. To visualize the centre B of the diffuse reflectance Δx away from the incident laser beam position (A), several intensity thresholds are used.

composed from known particular components[11]. We used the following relations between the reduced scattering coefficient μ'_s and the scattering cross-section C_{sc} [9,10]

$$\mu'_s = NC_{sc}(1\text{-}g) \tag{2}$$

where N is the number of spherical particles per unit volume having diameter d.

The value of N has been calculated from the respective volume fraction and the volume of the single particle. The effective refractive index of the medium reflects the change in the refractive index of the matrix due to the presence of the minor phase.

It is very well known that an ordered arrangement of similar particles of an optically isotropic material can display anisotropic optical properties (form birefringence). For an assembly of plates or thin rods in the surrounding medium one can determine effective refractive indices for incident field with its electric vector parallel with or perpendicular to the plate ($n_{p,II}$, $n_{p,\perp}$) (or $n_{r,II}$, $n_{r,\perp}$ for the rods).

For the thin rods we have[11]

$$n_{r,II}^2 = v_1 n_1^2 + v_2 n_2^2 \tag{3a}$$

$$n_{r,\perp}^2 = n_2^2\, ((1 + v_1)\, n_1^2 + v_2 n_2^2))/((1 + v_1)\, n_2^2 + v_2 n_1^2)) \tag{3b}$$

where v_1, v_2 are the volume fractions occupied by the rods and by the surrounding medium, respectively, and n_1, n_2 are the refractive indices of the minor phase (rods) and the polymer matrix, respectively.

Thus Eq. (1) can be used with the refractive index equal to the corresponding refractive index of rods depending on the particular arrangement of minor phase domains. Equations (1) and (3a,b) then form a basis for experimental determination of μ'_s parameters.

For calculation of theoretical values of μ'_s for oriented samples we used the following three procedures (i) concept of equivalent sphere[12], (ii) approximation of spheroidal particles[13] and (iii) complex analysis[14].

(i) For spheroids and ellipsoids not very different in shape from a sphere, the concept of equivalent sphere can be used. For a spheroid with semi-axis a, b, Eq. (4) holds[12]

$$(\mathrm{k}a)_{spheroid} = (\mathrm{k}a)_{sphere}(a/b)^{2/3} \tag{4}$$

(ii) Approximate solution of the light scattering problem has been recently presented for various orientation of spheroids with respect to the direction of incident light. Eq. (5)[13] reads

$$\mu^{II}_{spheroid} = \mu_{sphere}(b, n');\ n' = \mathrm{f}\,(a/b, n_1, n_2) \quad \mu^{\perp}_{spheroid} = (a/b)\ \mu_{sphere}(b, n'');\ n'' = \mathrm{f}(n_1, n_2) \tag{5}$$

where $\mu^{II}_{spheroid}$ is the scattering coefficient of spheroidal particles with their longer axes oriented parallel to incident light beam. Similarly, $\mu^{\perp}_{spheroid}$ is the same parameter for particles with spheroid axes oriented perpendicular to the incident light beam.

Experiment

To test Eq. (1), we used a video reflectometer[5,6] to measure the diffuse reflectance from a series of samples made of (i) polypropylene composites (Table 1) and (ii) oriented PMMA/PC composites (Table 2).

(i) Standard dumb-bell test specimens made of neat polypropylene Mosten 58412 (Chemopetrol, Czech Republic) filled with various amounts of EPDM particles (Table 1) with cross-section 10×4 mm (thickness) were used. The laser beam for the experiments with unoriented samples had an elliptic shape on the surface of the turbid medium and hence had a mirror symmetry about the y axis (perpendicular to x in Fig. 1). Figure 1 illustrates a diffuse reflectance pattern of sample PPR1 with thresholding to visualize better (in a wider surface area) the shift $\Delta x = x(B) - x(A)$ between the centre of the incident laser beam A and the centre of the diffuse reflectance B.

(ii) Standard dumb-bell specimens made of PC/PMMA composites (Table 2) were tested. We used polycarbonate SINVET 221 with various amounts of PMMA VEDRIL 9D of cross-section 10×4 mm (thickness). Light from a He-Ne laser (output 10 mW, wavelength $\lambda = 632.8$ nm) attenuated by a neutral filter and focused by lens (focal length f = 180 mm) was directed to the medium surface at the angle of incidence $\alpha_i = 80°$. The diffuse reflectance was measured with a 8-bit video CCD camera Pulnix 765, the images were computer-collected and then analyzed using the LUCIA D system[15].

Table 1. Parameters of studied PP/EPDM composites

Polymer composite	Volume of EPDM particles (%)	Refractive index[a)] n_m
PPR0	0	1.5108
PPR1	7.6	1.5072
PPR2	15.3	1.5053
PPR3	22.5	1.5035
EPDM	100	1.4847

[a)] At 632.8 nm.

Table 2. Parameters of studied PC/PMMA composites

Polymer composite	Volume of PMMA (%)	Refractive index[a)]	
		$n_{r,II}$	$n_{r,\perp}$
KOL15	5	1.5806	1.5809
KOL16	10	1.5752	1.5758
KOL17	15	1.5698	1.5707
KOL18	20	1.5646	1.5656
KOL19	30	1.5542	1.5556

[a)] n(PMMA) = 1.4868, n(PC) = 1.5860 both at λ = 632.8 nm.

Results and discussion

The experimentally obtained μ'_s and calculated values of reduced scattering coefficients for various diameters of EPDM particles at appropriate volume fractions are plotted in Fig. 2. It can be inferred from Fig. 2 that the reduced scattering coefficients of EPDM particles in the polypropylene matrix strongly depend on their diameters and concentrations; for the studied system, the diameter d = 0.6 μm is in a perfect accord with experimental data. The image analysis of SEM images indicated that the size values obtained by μ'_s measurements are in reasonable agreement with those from SEM images. It should be noted that the light scattering data are collected from much larger volumes (ca 10^4–10^6 times) than the single SEM image and thus are representing much more "averaged" size parameters.

The unoriented isotropic character of the studied samples is illustrated in Fig. 3, where one can see the thresholded images with incident light oriented along and perpendicular to the long axis of the dumb-bell shaped samples. Evaluation of oriented PMMA/PC samples has been carried out in the fixed orientation, with incident light parallel to the long axis of the sample. The thresholded image of the sample KOL16 is given in Fig. 4.

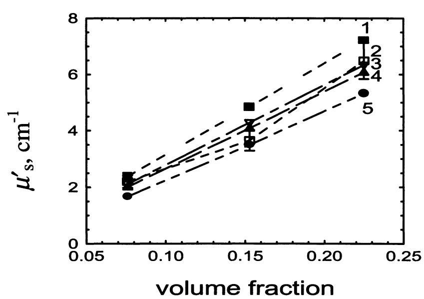

Fig. 2: Reduced scattering coefficients μ'_s for various diameters d of EPDM particles in PP matrix (calculated data) and for composites PPR1, PPR2 and PPR3 (experimental, with error bars) d in μm: *1* ■ 0.5, *2* ∇ 0.6, *3* □ experimental data, *4* Δ 0.7, *5* ● 1.

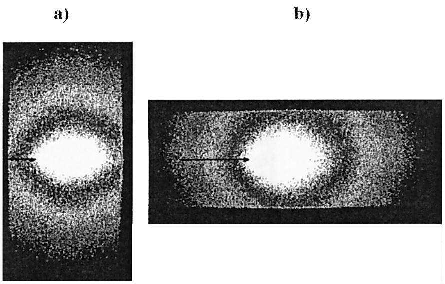

Fig. 3: A diffuse reflectance pattern obtained with composite PPR3 (Table 1). Several thresholds are used to visualize the slight asymmetry of the pattern. The shift Δx for unoriented samples does not depend on the direction of the incident laser beam.

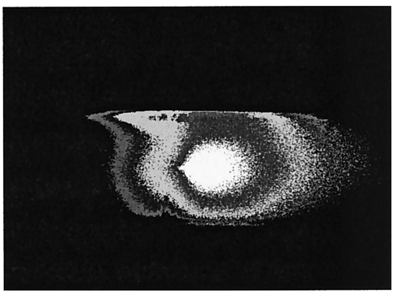

Fig. 4: A diffuse reflectance pattern obtained from KOL16 (Table 2). Several thresholds are used to visualize the asymmetry of the diffuse reflectance far from the incident laser beam. Nonhomogeneity of the pattern at the rim of the sample is clearly discernible. The incident laser beam is oriented parallel to the long axis of spheroids.

Using the refractive indices $n_{r,II}$, the μ'_s value has been determined from Eq. (1) for the series of PMMA/PC composites from Table 2. It should be noted that the thresholded image (Fig. 4) clearly displays some nonhomogeneity in orientation at upper rim of the sample and gives thus information about homogeneity of orientation (skin-core effect). The smaller cross-section dimensions (b dimension of prolate spheroid) calculated from experimental μ'_s data are given in Fig. 5 and compared with values obtained from SEM images (cf. Table 3).

Table 3. Parameters of studied samples PC/PMMA: dimensions, anisometry, equivalent sphere dimension $(kb)_{sphere}$ (from image analysis of EM pictures)

Composite	$x = (kb)_{sphere}$	Dimension $2a$ (μm)	Dimension $2b$ (μm)	Anisometry a/b
KOL15	2.08x	0.30	0.1	3:1
KOL16	3.41x	0.43	0.081	5.3:1
KOL17	3.37x	0.47	0.091	5.2:1
KOL18	6.35x	1.8	0.125	14:1
KOL19	9.44x	5.7	0.15	38:1

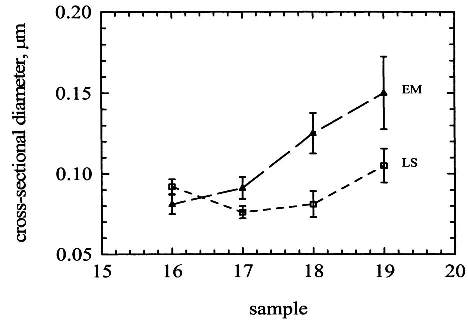

Fig. 5: Comparison of the cross-section diameters *d* of PMMA/PC composites (Table 2) from experimental μ'_s values and from image analysis of EM pictures. □ light scattering data, Δ EM analysis dimension.

As stated earlier, the number of polydisperse spheroidal domains included in light scattering measurement is much higher than that in SEM analysis. A perfect accord of both values could not be expected due to a principally different order of averaging of polydisperse domains by the used methods. Nevertheless, both the methods indicate only a small increase in cross-section dimensions and the volume increase of the minor PMMA phase manifests itself by an increase in longitudinal dimensions *a* (cf. Table 3).

The thresholded images of oriented composite KOL16 at increasing angle of incident light and longitudinal axis of the sample are presented in Fig. 6. The whole extent of possible orientations, from incident light parallel to long axis of the sample (position 0°) to that with perpendicular orientation (position 90°) is presented. The information content of such images with regard to orientation of samples is remarkable.

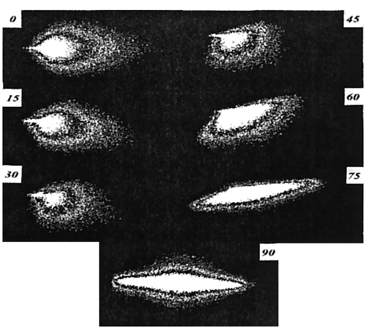

Fig. 6: A diffuse reflectance patterns obtained for various orientations of composite KOL16 (Table 2) with respect to the incident laser light. Several thresholds are used to visualize their asymmetry. The increasing angle between the direction of the incident laser light and the long axis of the sample (parallel to the long axes of the spheroids) is clearly discernible. Positions 0° and 90° correspond to the parallel and perpendicular orientations of both axes.

The results can be summarized as follows:

(a) The laser beam diffuse reflectance can be used to measure reduced scattering coefficients μ'_s of polymer composites in the multiple-scattering regime.

(b) The experimentally obtained μ'_s values are consistent with the values calculated using the Lorenz-Mie theory in the diffusion approximation.

(c) A reasonable agreement has been found between size parameters obtained by the diffuse reflectance method and by direct image analysis of the SEM images.

(d) The concept of LS by an equivalent sphere is not appropriate for the description of oriented samples.

(e) Replacement of elongated minor phase domains (particles) with spheroids and use of the LS theory gives parameters similar to those obtained from EM images (for orientation parallel to the long axis of the spheroids).

(f) Orientation of the optical axes of the specimens can be evaluated from the thresholded images.

(g) First attempts to describe the LS of arbitrary oriented particles in polymer matrix are promising.

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References

[1] L. Utracki, R.A. Weiss (eds.), *Multiphase Polymers: Blends and Ionomers*, ACS Symp.Ser. 395 (1989)
[2] H. C. van de Hulst, *Multiple Light Scattering*, Vol.1, 2, Academic Press, (1980)
[3] G. H.Meeten, Ed., *Optical Properties of Polymers,* Elsevier Appl. Sci. Publ. London, 1986
[4] V. Twersky, *J. Op. Soc. Am.* **52,** 145 (1962)
[5] L. Wang, S. L. Jacques, *Appl. Opt.* **34,** 2362 (1995)
[6] J. Holoubek, *Polymer* **40**, 277 (1998)
[7] M. Kerker, *The Scattering of Light*, Academic Press, New York, 1980
[8] R. Graaff, J. G. Aarnoudse, F. F. M. de Mul, H. W. Jentink, *Appl. Opt.* **28,** 2273 (1989)
[9] J. Holoubek, *Opt. Eng.* **37**, 705 (1998)
[10] J. Holoubek, J. Kotek, M. Raab, *Polym. Bull.* **37,** 631 (1996)
[11] M. Born, E. Wolf, *Principles of Optics*, Pergamon Press, Oxford 1964, p.707
[12] P. W. Barber, S. C. Hill, *Light Scattering by Particles*, Chap. 3, Word Sci. Publ., Singapore 1990, p.103
[13] T. W. Chen, L. M. Yang, *Opt. Commun.* **123**, 437 (1996)
[14] J. P. Barton, Proceedings 5th Int. Congress *"Optical Particle Sizing"*, 10-14 Aug.1998, Minneapolis, p.45
[15] LUCIA D, system for image processing and analysis, http://www.lim.cz