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Light scattering and reflectance of optically heterogeneous polymers in multiple scattering regime

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Abstract

A simple approach is used to measure the reduced scattering coefficient μ_s' of a thick turbid medium having a small absorption coefficient $\mu_a' \ll \mu_s'$. Based on the light reflectance measurement of semi-infinite media by means of a CCD camera, the value of shift Δx between the centre of the incident laser beam and the centre of the diffuse background is determined, which is inversely proportional to the μ_s'. The experimental values of μ_s' determined for EPDM particles in a polypropylene matrix are compared with model calculations using the Lorenz–Mie theory. A comparison of theoretical data with parameters from image analysis of SEM pictures gives good accord. © 1998 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Real polymeric materials inevitably contain defects and heterogeneities of different nature and origin. They can be intrinsic (semicrystalline polymers), intentionally introduced (polymer blends) or developed under mechanical stress (i.e. in stress-whitening process). A great majority of blends are immiscible from the thermodynamic standpoint and also most 'blends of commerce' are immiscible. Such blends form a multi-phase system with a deformable minor phase and, under appropriate conditions, morphological structures such as spheres, ellipsoids, fibres, and plates can be produced. Under certain conditions, co-continuous phases may also be formed [1,2]. 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 transparent or translucent materials because they are noninvasive, rapid and applicable to high-temperature materials. A limitation of conventional light-scattering techniques is their requirement of relatively thin samples in order to avoid multiple scattering effects [3–5]. The approach described in this paper is proposed to circumvent this limitation; as a result, a semi-infinite material may be inspected with access to a single side of the material.

Recently, a hybrid model of the Monte Carlo (MC) simulation and diffusion theory has been described, which combines the accuracy advantage of MC simulation and the speed advantage of diffusion theory being, at the same time, faster than pure MC simulation and more accurate than the pure diffusion theory [6,7]. Roughly, MC simulation is used initially to describe the propagation of photons to sufficient depth into the turbid media (collecting some reflectance R_{MC} that is due to near-surface scattering). Diffusion theory is then used to compute the reflectance R_{diff} distant from the source. The final reflectance R_d will be the sum of the two reflectances. The application of the above-mentioned method to polypropylene samples with various amounts of ethylene–propylene rubber particles (EPDM) is presented here. 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.

2. 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 the anisotropy factor [8] g. The relative refractive index n_r is the ratio between the refractive indices of the turbid medium and of the 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

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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 [8–10].

For a semi-infinite medium whose $\mu_a \ll \mu_s$, a simple and rapid approach to measure the reduced scattering coefficient, $\mu_s' = \mu_s(1 - g)$, has been derived [6,7]. 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 an amount Δx. This amount is used to compute μ_s' by

$$\mu_s' = \sin \alpha_i/(n_r \Delta x) \quad (1)$$

The following subsections describe the experimental testing of Eq. (1) and a comparison with the 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 composed from known particular components [11]. The calculations of the Lorenz–Mie functions by means of Mie3 code [12] have been performed. We used the following relations between the reduced scattering coefficient μ_s' and the scattering cross-section C_{sc} [11,13]

$$\mu_s' = NC_{sc}(1 - g) \quad (2)$$

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 refractive index of the matrix due to the presence of the minor phase. Even if the scattering arises principally from the fluctuating part of the index (index mismatch between scatterer and immediate environment), the fact that the relative refractive index of the particle must decrease as the volume fraction of the minor phase increases is generally accepted and very well verified experimentally [4,8]. The concentration dependence of the refractive index of the medium (effective refractive index of matrix), n_m, has the form of the modified mixing rule [4,14]

$$n_m = n_1 + v_1(n_2 - n_1)\Psi \quad (3)$$

where n_1, n_2 are refractive indices of both phases, v_1 is the volume fraction of the minor phase and Ψ is a correcting factor depending on the relative refractive index n_1/n_2 and on the size of the particle relative to the wavelength [14].

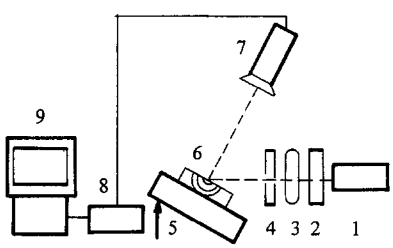

Fig. 1. Schematic diagram of the video reflectometer. (1) Laser, (2) attenuation filter, (3) objective lens, (4) diaphragm, (5) tilting stage, (6) sample, (7) CCD camera, (8) CCD controller, (9) computer.

Table 1
Parameter values of studied samples

Sample	Fraction of embedded EPDM particles (%)	Refractive index n_m (λ = 632.8 nm)
PPR0	0	1.5108
EPDM	100	1.4847
PPR1	7.6	1.5072
PPR2	15.3	1.5053
PPR3	22.5	1.5035

3. Experiment

To test Eq. (1) experimentally, we used a video reflectometer [6,15,16] (Fig. 1) to measure the diffuse reflectance from a series of samples made of polypropylene composites (Table 1). Light from a He–Ne laser (output 10 mW, wavelength λ = 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 α_i = 80°. An 8-bit video CCD camera Pulnix 765 measured the diffuse reflectance, and the computer collected and then analysed the image using the LUCIA D system [17]. The dynamic range of the CCD camera is limited to 255 intensity levels. Therefore, two images with different laser beam intensities were taken to measure the diffuse reflectance in a wider surface area. The laser beam for this experiment has an elliptic shape on the surface of the turbid medium, and hence has a mirror symmetry about the y-axis (perpendicular to x in Fig. 2). Fig. 2 illustrates a diffuse reflectance pattern for sample PPR1 with thresholding to visualize better 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 in a wider surface area. Standard dumb-bell test specimens were used with the parameters given in Table 1. We used neat polypropylene Mosten 58412

Fig. 2. A diffuse reflectance pattern obtained with a CCD camera from sample PPR1 (Table 1). Several thresholds are used to visualize the centre B of the diffuse reflectance far from the incident laser beam (position A). A shift away Δx is indicated. The scale bar is 1 mm.

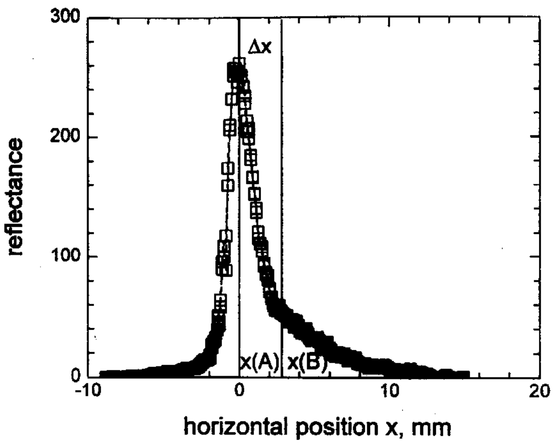

Fig. 3. Diffuse reflectance along the x-axis for the PPR1 sample; shift $\Delta x = x(B) - x(A)$. The resolution of the image was 6.3×10^{-3} cm/pixel.

Table 2
Shift values Δx and corresponding reduced scattering coefficients $\mu_s{}'$

Sample	Δx (cm)	$\mu_s{}'(n_m)$ (cm^{-1})	$\mu_s{}'(n_m)$ (cm^{-1})
PPR1	0.298 ± 0.006	2.20 ± 0.07	2.20 ± 0.07
PPR2	0.190 ± 0.006	3.45 ± 0.17	3.44 ± 0.17
PPR3	0.101 ± 0.006	6.5 ± 0.6	6.4 ± 0.6

(Chemopetrol, Czech Republic), cross-section 10 × 4 mm (thickness) filled with various amounts of particles (EPDM).

4. Results and discussion

Fig. 3 shows the measured diffuse reflectance for sample PPR1 along the horizontal central line crossing from A to B in Fig. 2 as function of x. The peak reflectance occurred at the centre of the incident laser beam and defined the A position. The central point of the circular periphery that is several transport mean-free paths away from the incident point defined the apparent centre B. The difference $x(B) - x(A)$ yielded the offset value Δx. We usually used two measurements, with and without the attenuation of the laser source intensity, to obtain a sufficient dynamic range of the reflectance. The resolution in the setup was 6.3×10^{-3} cm/pixel, and the experimental error was ca. 1 pixel. The results are summarized in Table 2.

The reduced scattering coefficients in Table 2 are calculated using Eq. (1), where the refractive index n_m is taken from Eq. (3) with $\Psi = 1$ for the last but one column and n_m for the last column is determined for EPDM particles with diameter $d = 0.6$ μm according to Nakagaki and Heller's theory [14]. As can be seen, the difference in reduced scattering coefficients thus calculated is very small and is within an experimental error. The experimentally obtained $\mu_s{}'$ and calculated values of reduced scattering coefficients for various diameters of EPDM particles at appropriate volume fractions are plotted in Fig. 4. It can be inferred from Fig. 4 that the reduced scattering coefficients of EPDM particles in the polypropylene matrix relatively strongly depend on their diameters and concentrations; for the studied system, the diameter $d = 0.6$ μm is in the best accord with experimental data. The SEM image of the PPR2 sample presented in Fig. 5 indicates that the size value obtained by means of $\mu_s{}'$ measurement is in reasonable agreement with the SEM image. It is very well known that light scattering measurements in polydispersions usually give apparently larger sizes than 'true' distribution. To support the last assertion, the size distribution given in the inset of Fig. 5 has been used for calculation of the total reduced scattering coefficient $\mu_s{}'$. The result given in Fig. 6 indicates the prevailing role of the large diameters in the total $\mu_s{}'$. It should be noted that the light scattering data are obtained from much larger three-dimensional space than the single 'realization' of the taken in the SEM image.

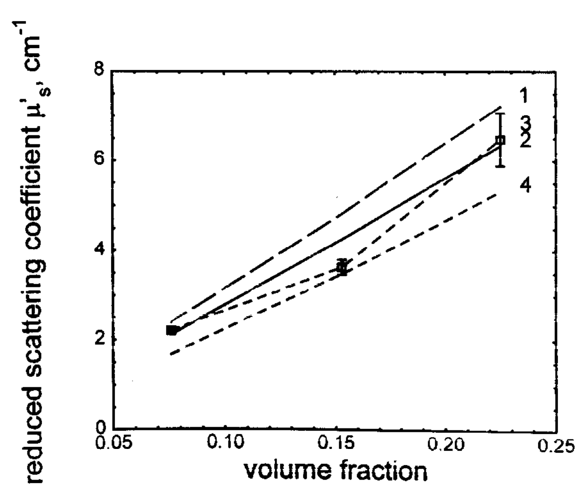

Fig. 4. Comparison of reduced scattering coefficients $\mu_s{}'$ for various diameters d of EPDM particles in polypropylene matrix (theoretical data) and $\mu_s{}'$ values for samples PPR1, PPR2 and PPR3 (experimental data). (1) $d = 0.5$ μm (— — —); (2) $d = 0.6$ μm (——); (3) (□) experimental data with error bars; (4) $d = 1$ μm (- - -).

The results can be summarized as follows:

(a) the laser beam diffuse reflectance can be used to measure reduced scattering coefficients $\mu_s{}'$ of polymer composites in the multiple-scattering regime;

(b) the experimentally obtained $\mu_s{}'$ values are in good accord with the values calculated by means of 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.

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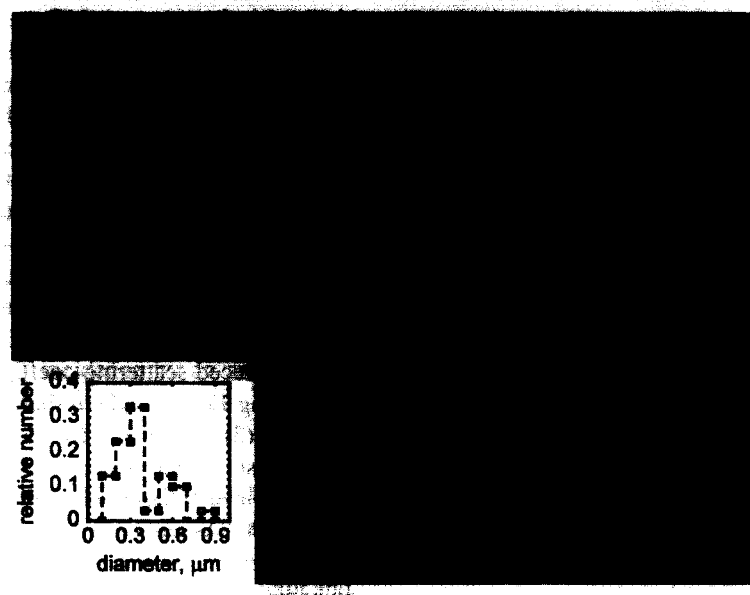

Fig. 5. SEM image of PPR2 sample. A histogram of the size distribution (diameters in μm) of EPDM particles obtained by image processing is given in the inset (the scale bar is 1 μm).

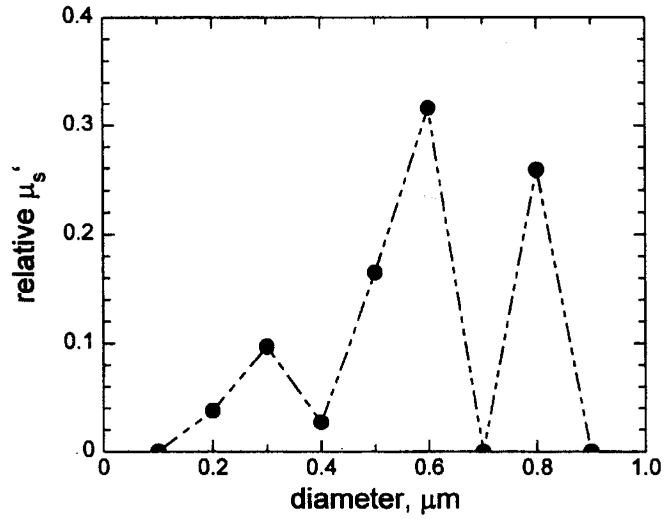

Fig. 6. Relative contributions of the various diameters from the SEM image of PPR2 sample (cf. histogram in the inset of Fig. 5) to the total reduced scattering coefficient μ_s'.

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