Precise measurement of rubber membrane thickness in high-impact polystyrenes

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Polystyrene (PS) belongs among the four most common plastics (LDPE, HDPE, PP, PS). World production of PS is higher than 20 Mt/year; more than 50 % of PS is produced in the form of high-impact polystyrene (HIPS), which consists of PS matrix with rubber particles. Main component of rubber is usually polybutadiene (PB). HIPS typically contains 1-10 wt % of rubber that increases impact strength of the material ca 10-20×. HIPS polymers exhibit typical salami morphology (Fig. 1): PS matrix contains rubber particles, which partially encapsulate PS. Two facts are important for HIPS production: (i) PB is more expansive than PS and (ii) rubber particles with costly PB have approximately the same effect, regardless of the PS encapsulation. Therefore, HIPS polymers with thick membranes in rubber particles (Fig. 1a) are less competitive than those with thinner membranes (Fig. 1b).

Thickness PB membranes can be estimated from chemical analyses, spectroscopic experiments or directly measured from STEM micrographs (Fig. 1ab). These methods are either laborious (chemical methods) or imprecise (spectroscopy, direct measurements). Low precision of the direct measurements on STEM micrographs results from two facts: (a) the membranes are usually so thin that they occupy just a few pixels on digitized micrographs – this leads to high measurement errors and (b) the direct measurement is vaguely defined – it is not clear where and how many times to measure a membrane.

In this study, we introduce an alternative, semi-automated image analysis method for determination of thickness of rubber membranes. The method is based on determination of PS volume in rubber particles. At first step, STEM micrographs (Figs. 1ab) are converted to binary images (Figs. 1cd) using a standard image analysis software. At second step, we employ the key formula of stereology (Eq.1, ref. [1]), which says that areal fraction A_A, determined on sections through a volume, represents an estimate of the volume fraction V_V of the phase under investigation. In our case we measure one image analysis parameter: $\langle FR \rangle = \langle FillRatio \rangle$ (Eq.2, ref. [2]), which is an average ratio of area covered by holey rubber particles (parameter *Area* in Eq.2) and area covered by filled rubber particles (parameter *FillArea* in Eq.2). Combination of Eq.1 and Eq.2 leads to the conclusion that thickness of rubber membranes T_M is proportional to the average volume fraction of rubber in the particles (Eq.3); in case of 1μm spherically symmetric core-shell particles the T_M is given by Eq.4.

$$V_V = A_A \quad \text{(Eq. 1)}$$

$$\langle FR \rangle = \langle FillRatio \rangle = \langle Area \,/\, FillArea \rangle \quad \text{(Eq. 2)}$$

$$T_M \propto \langle FR \rangle \quad \text{(Eq. 3)}$$

$$T_M = 1 - (1-\langle FR \rangle)^{1/3} \quad \text{(Eq. 4)}$$

The average thicknesses of rubber membranes, based on Eq.3-4, were determined from six different HIPS polymers, including the two types shown in Fig.1. The polymers

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were either commercially available or they came from the laboratory at company SYNTHOS Kralupy a.s. within a common research project [3]. For each sample, four independent STEM micrographs with the same magnification were analyzed. It has been demonstrated that the T_M values correlated well with the chemical analyses results. Within each HIPS sample, the estimated standard deviations of T_M were lower than 10 % of final values. When comparing different HIPS samples, the final values of T_M were significantly different according to two-sample t-test. To conclude, the image analysis technique, which determines thickness of rubber membranes from volume of encapsulated PS particles, is more precise than direct measurement and can be successfully used for investigation and/or comparison of HIPS structures.

1. E.E. Underwood, Quantitative Stereology. Adison-Wesley, London 1970. pp. 25-27.
2. NIS Elements software (Laboratory imaging, Czech Republic, www.lim.cz).
3. Financial support by the Czech Ministry of Industry and Trade (project FT-TA3/110) is gratefully acknowledged.

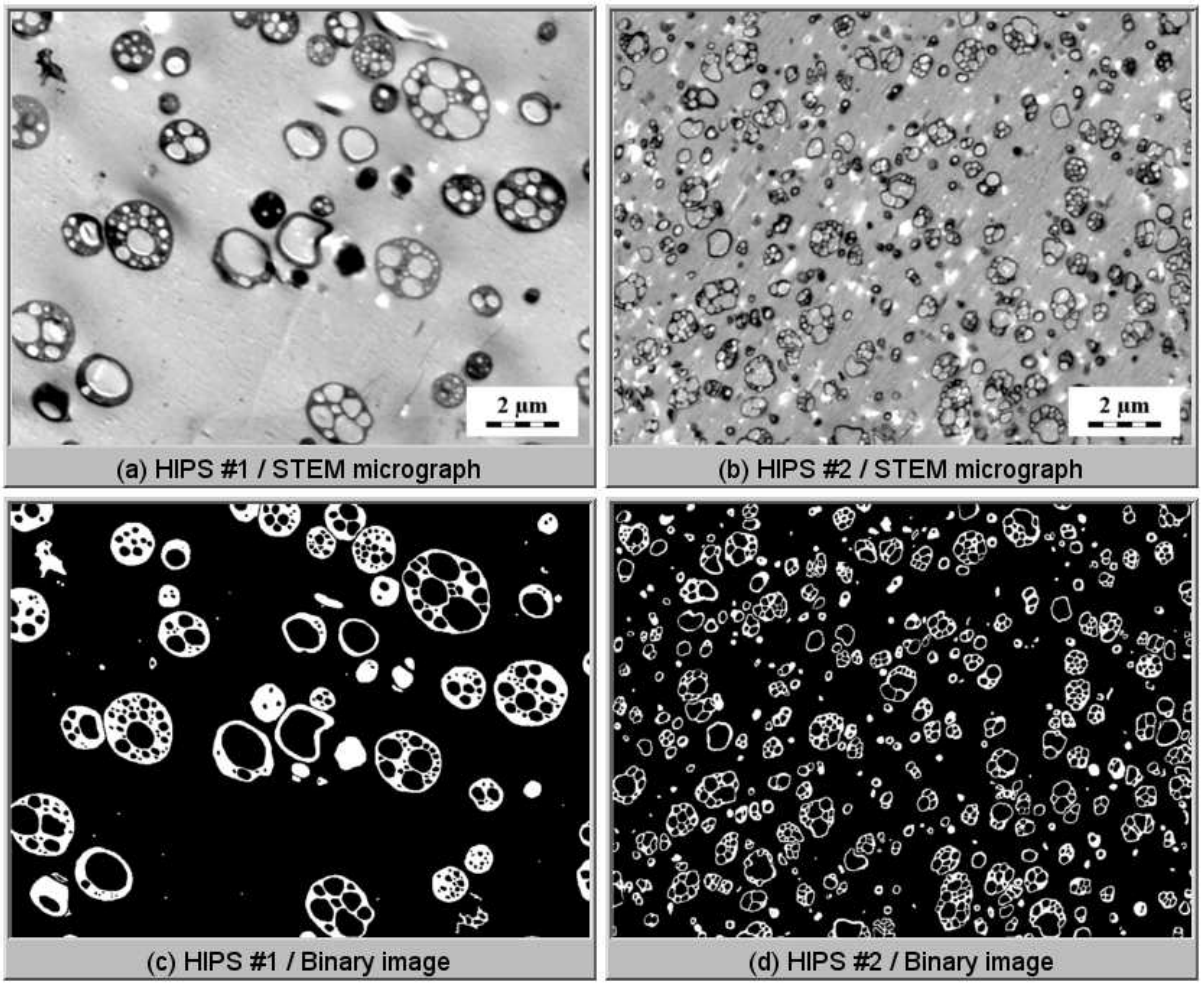

Figure 1. Two different types of high-impact polystyrenes, denoted #1 and #2. (a,b) STEM micrographs of OsO_4-stained ultrathin sections, showing dark rubber particles in light PS matrix. (c,d) Binary images corresponding to the STEM micrographs above, which were used as an input for image analyses.

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