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Test method

Morphological analysis of polymer systems with broad particle size distribution

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ABSTRACT

This contribution is focused on precise determination of particle size distribution in polymer blends with complex morphology by means of our new program called MDISTR. Standard determination of the particle size distribution is usually achieved by measurement of particle sizes in (a single set of) electron micrographs. We show why this method fails for two frequent cases: (i) blends with very broad particle size distribution and (ii) blends that are composed of domains with different particle sizes. On real-life examples, we demonstrate that program MDISTR yields accurate particle size distributions in both the above-mentioned cases, while the standard image analysis gives average particle sizes differing by >100 % from the correct result. We describe MDISTR calculations which are based on a linear combination of standard particle size distributions from two (or more) sets of micrographs with different magnifications, different locations within the sample and precisely defined statistical weights.

1. Introduction

The properties of immiscible polymer blends are controlled, besides from their composition and the properties of their components, by their phase structure/morphology [1]. Therefore, a precise description of polymer blend morphology is required for predicting, tailoring and fine-tuning the blend properties [1–3]. Moreover, the accurate quantitative descriptors of the blend morphology are also needed for better understanding of the phase structure evolution during blend preparation and processing [4,5].

For blends having droplets-in-matrix morphology, the average droplet size and the width of droplet size distribution are the parameters that correlate with the blend properties qualitatively [1]. These parameters are mostly determined from randomly chosen microphotographs containing together 10^2–10^3 of droplets [6]. This method provides reasonable results for blends having uniform phase structure, but it fails for blends containing domains with different average droplet sizes or droplets with very broad size distribution, when the difference between the smallest and the biggest droplet becomes higher than one order of magnitude, as discussed and demonstrated below.

The number of polymer blends that exhibit broad particle size distribution is surprisingly high. In polymer blends with low interfacial tension and high viscosity ratio, the coexistence of zones with big particles and zones with substantially smaller particles was shown to be quite common [7–12]. Large zones (with size in the range of hundreds of μm), differing clearly in the average particle size, were also detected in polystyrene/low-density polyethylene blends [2,13], polystyrene/polyamide and polyethylene/cycloolefin copolymer blends [6], and in a number of various polypropylene/polystyrene blends [14–17]. It has been shown that evaluation of the different zones of these blends, containing several hundreds of particles, provides strongly different average particle sizes. This clearly illustrates that the application of a common method of

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determination of the average particle size to these blends can lead to totally misleading conclusions [6]. Other polymer systems, such as some grades of high-impact polystyrene [18], may have bimodal particle size distribution. In these cases, determination of the particle size distribution by evaluation of the area containing ca 10^2–10^3 particles is insufficient for obtaining results which can be quantitatively correlated with the blend properties [18]. An extension of the particle size evaluation to the areas containing 10^4–10^5 particles would be both inefficient (too laborious and time consuming) and ineffective (it would fail due to different statistical weights of small and big particles on high and low magnification micrographs, as exemplified below).

This contribution is focused on precise quantification of polymer blend morphology in more difficult cases, when the particle size distribution is very broad and/or when the blend contains zones with different particle size distributions. We describe a new, more precise method of particle size analysis, based on combination of data from several sets of micrographs that have different magnifications (if the particle size distribution is broad) and/or locations on the sample (if the sample is inhomogeneous). The particle sizes from each individual micrograph are assigned correct statistical weight before the final size distribution is calculated; the weights of the micrographs are essential for correct calculation and depend on the number of micrographs, on their magnification and on the analyzed area. As the calculations deal with huge amounts of numbers, the algorithm was implemented in our new program MDISTR, which makes the image analysis of difficult systems more feasible and user-friendly. We demonstrate on two typical cases how much the MDISTR improves the accuracy of the particle size distributions in comparison with standard image analysis procedures.

2. Experimental

2.1. Materials

Two polymer systems were analyzed: high-impact polystyrene (HIPS) and a blend of polylactic acid with polycaprolactone (PLA/PCL). Both materials exhibited particulate structure with very broad particle size distribution.

2.1.1. HIPS polymer

HIPS is an elastomer modified polystyrene thermoplastic. It is a two-phase system, consisting of polystyrene (PS) matrix that contains complex-morphology elastomer particles (formed by addition of *cis*-polybutadiene, PB). The investigated HIPS polymer was a commercial product of Synthos Kralupy a.s. (Kralupy nad Vltavou, Czech Republic). It has been produced in a small-scale batch (batch designated BD1, with optimized impact strength = 12.6 kJ/m^2, produced in 2008), which contained both very large and very small PB particles (particle size varied within two orders of magnitude, from 0.1 μm to 10 μm).

2.1.2. PLA/PCL polymer blend

PLA/PCL blend was composed of two bio-based polymers: polylactic acid (PLA; Biopolymer 4032D, NatureWorks LLC, USA; MFI = 6.3 g at 210 °C/2.16 kg) and polycaprolactone (PCL; Capa 6800; Perstorp Holding AB, Sweden; MFI = 5.7 g at 210 °C/2.16 kg). The blend was prepared in a wide range of compositions (from 90/10 to 50/50). The samples were produced by melt mixing (180 °C, 50 rpm, 10 min) inside the chamber B 50 EHT of a Brabender Plasticorder (Brabender, Germany) and then compression molded (180 °C, 10 min, 220 kN) by hydraulic press (Fontijne Grotnes, Netherlands). In this work, we analyzed the 70/30 blend, with the most inhomogeneous particulate structure (zones with smaller or bigger particles) and the broadest particle size distribution (ranging from submicrometer-sized particles to 15 μm).

2.2. Electron microscopy

2.2.1. Scanning electron microscopy

Scanning electron microscopy (SEM) was performed with a Vega TS 5135 microscope (Tescan, Czech Republic) using secondary electron imaging at 30 kV. For the microscopic observation, both HIPS and PLA/PCL samples were cut from the compression molded specimens, their surfaces were smoothed under liquid nitrogen [19] and then etched in order to visualize particle morphology. In the case of HIPS, we applied etching with permanganic mixture (0.4 g $KMnO_4$ in 10 cm^3 of conc. H_2SO_4 and 10 cm^3 of conc. H_3PO_4). After etching, the samples were thoroughly washed in running water. In the case of PLA/PCL blends, we etched the samples with tetrahydrofuran vapor at 45°C for 4 min. Before observation in the electron microscope, the smoothed and etched surfaces were fixed on a metallic support using conductive double-adhesive carbon tape (Christine Groepl, Austria), further fixed with conductive silver paste (Leitsilber G302, Christine Groepl, Austria) and sputtered with Pt (vacuum sputter coater, SCD 050, Balzers, Germany) in order to minimize charging and sample damage.

2.2.2. Scanning transmission electron microscopy

The scanning transmission electron microscopy (STEM) of the HIPS polymer was performed with a Vega TS 5135 microscope (Tescan, Czech Republic) equipped with a transmission adapter, using transmitted electrons imaging at an acceleration voltage of 30 kV. The ultrathin sections (60nm) for the STEM observation were prepared by ultramicrotomy (ultramicrotome Ultracut UCT, Leica, Germany) at cryo-conditions (the sample and knife temperatures were −70 °C and −50 °C, respectively). The ultrathin sections were transferred on a microscopic grid and stained with OsO_4 vapor for 1.5 h in order to contrast double bonds in PB polymer.

2.3. Program MDISTR: calculation of precise particle size distributions

The calculation of particle size distribution was performed using our own program MDISTR, which is introduced in this work. The program calculates and/or simulates various 2D and/or 3D particle size and/or morphology distributions. It is optimized for processing more difficult samples, in which the standard image analysis fails (as demonstrated below in the Results section).