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Low-voltage TEM imaging of polymer blends[☆]

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Abstract

Low-voltage transmission electron microscopy (LV-TEM) was applied to obtain images of the phase structure of selected polymer blends without any prior staining. The instrument used (LVTEM-5, working at 5 kV) is of a novel construction combining visual-light and electron-microscopical techniques, resulting in an enhanced efficiency of light transport to the eye and facilitating CCD imaging. Results were compared with LV-STEM at 25 kV. Phase structure of polycarbonate/poly(styrene-*co*-acrylonitrile) (PC/SAN), polystyrene/polypropylene (PS/PP), and polyethylene/polypropylene blends (PE/PP, ADFLEX) were selected to demonstrate the above techniques. The difference in density between the individual components of polymer blends was found to be the reason for the obtained image contrast. Differences less than 0.04 g/cm^3 can be traced with this technique. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Low-voltage transmission electron microscopy; Polymer blends; Polycarbonate blends

1. Introduction

Information on the phase structure of polymer blends is crucial for understanding the mechanisms of their behaviour (mechanical properties, modifications, compatibilization). The phase structure (morphology) is therefore sought microscopically with the use of any preparation and observation technique applicable.

Theoretical studies of miscibility and compatibility of polymer blends can exploit a variety of preparation techniques ending with a thin film which can be observed directly. However, in all the studies of bulk material prepared from the melt, the internal structure of the test piece has to be revealed. Numerous techniques such as fracturing, cutting and etching are exploited in various combinations (cf. Refs. [1–3]). Fracture surfaces obtained in the mechanical tests at room temperature are observed, in addition to those prepared in cryogenic conditions, and those with some component(s) removed by selective dissolution or chemical etching. Cut surfaces are observed after treatments like etching, selective dissolution or also after heat treatment [4]. The most frequently applied technique, though, is observation of stained ultrathin sections.

Slight differences in elemental composition of individual components of polymer blends do not usually allow adequate contrast to observe the phase structure of the blends to be achieved. Therefore, staining techniques are applied to enhance the contrast of ultrathin sections (cf. Ref. [5]). However, application of the ultrathin sectioning technique to some polymer blends may be very difficult and may involve some chemical treatment prior to the sectioning, which complicates the sample preparation and is usually time-consuming. Therefore, other techniques are sought.

In this contribution, transmission electron microscopy techniques are discussed that make it possible to observe the phase structure of the polymer blend from ultrathin sections without any other further treatment (staining).

2. Experimental

2.1. Materials

Polycarbonate/poly(styrene-*co*-acrylonitrile) (PC/SAN) binary blends of the compositions 50/50, and 75/25 (PC/SAN). The PC was bisphenol A polycarbonate SINVET 251 (ENI, Italy); density 1.20 g/cm^3; $M_w = 36,000$ g/mol, $M_n = 25,000$ g/mol. Styrene–acrylonitrile copolymer (with 24 wt% acrylonitrile) was Kostil AF 600 (ENI, Italy); density 1.07 g/cm^3; $M_w = 135,000$ g/mol, $M_n = 69,500$ g/mol Preparation of samples was described elsewhere [6,7].

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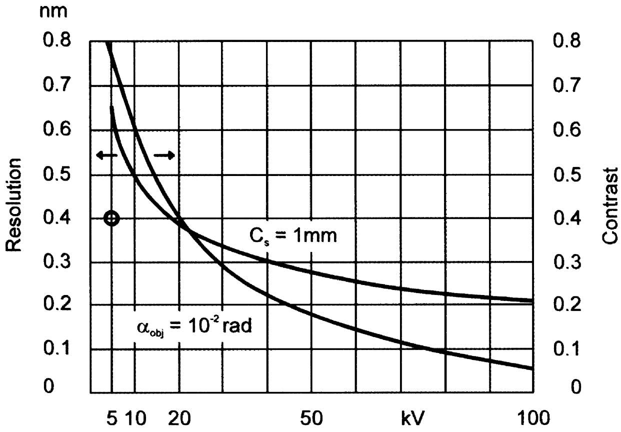

Fig. 1. Dependence of resolution and contrast of TEM on the acceleration voltage [11]. The dependence of contrast holds for a 20 nm thick carbon film; the resolution ($d = 0.43(C_s\lambda^3)^{1/4}$) is given for lenses with the same coefficient C_s= 1 mm.

Polystyrene/polypropylene (80/20) blend (PS/PP) [8]. Polystyrene was Krasten 151, (Kaucuk Comp., Kralupy, Czech Republic), $M_w = 330,000$, $M_n = 125,000$. Polypropylene was Mosten 52 592, commercial product of Chemopetrol a.s., Litvínov, Czech Republic; $M_w = 140,000$, $M_n = 85,000$.The blend was compatibilized with 5 pph of CARIFLEX TR1102 (Shell).

Polyethylene/polypropylene blends (PE/PP) [9]. Low-density polyethylene was Bralen RA 2-19, commercial product of Slovnaft a.s., Bratislava, Slovakia; $M_w = 120,000$, $M_n = 80,000$. Polypropylene was Mosten 52 592, commercial product of Chemopetrol a.s., Litvínov, Czech Republic; $M_w = 140,000$, $M_n = 85,000$.No compatibilizer was used.

Ethylene–propylene copolymer ADFLEX. Details of the material prepared in two steps are not known to authors.

2.2. Instrumentation

A low-voltage transmission electron microscope (LV-TEM) [10,11] of an original construction (LV TEM-5, Delong Instruments, Czech Republic) was applied, operating at an acceleration voltage about 5 kV.

A scanning electron microscope (JSM 6400, JEOL) with a transmission adapter (STEM) was applied, operating at an acceleration voltage not higher than 25 kV.

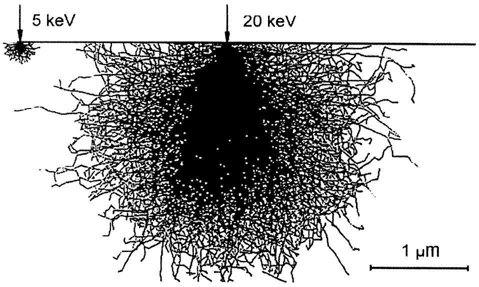

Fig. 2. Monte-Carlo simulation of electron trajectories in YAG–Ce single-crystal screen [11].

Ultrathin sections were cut using the ultramicrotomes Ultracut (Leica), or Ultrotome III (LKB). Very thin sections were cut at room temperature or in cryogenic conditions.

3. Results and discussion

3.1. Low-voltage transmission electron microscopy (LV-TEM)

The resolution of a transmission electron microscope (TEM) depends on the energy (wavelength) of the moving electrons: the higher the energy (given by the acceleration voltage) the better the resolution. On the other hand, the image contrast decreases with increasing energy of the electrons (Fig. 1) [10,11]. A low acceleration voltage was applied in order to obtain images of ultrathin sections of selected polymer blends with sufficient contrast without any prior treatment (staining).

Unlike the conventional voltage values around 100 kV used in transmission electron microscopy, a voltage of the order of units of kV is exploited in LV-TEM. At those voltages, the instrument is able to provide an enhanced imaging contrast nearly 20 times higher than for 100 kV, which is interesting especially for low atomic number specimens. The instrument used (LVTEM-5) is of a novel construction, combining electron-microscopical and visual-light microscopical techniques resulting in an enhanced efficiency of light transport to the eye and facilitating CCD imaging.

The low-voltage electron microscope is composed of two microscopes: a small electron microscope with magnification of maximum 250 times with a single YAG single-crystal fluorescent screen, and a standard high-quality commercial light microscope with magnification as high as 400 times. The total maximum magnification is approximately 100,000 times.

The above set-up of the microscope has several advantages. Compared with direct observation of the electron microscopical image on a conventional fluorescent screen, the instrument renders a high light transport efficiency: An amount of light 10,000 times higher comes to the eye through the objective lens with numerical aperture NA = 1 than to the naked eye from the fluorescent screen. At the used operating voltage of 5 kV, scattering of electrons in the YAG single-crystal detector is relatively low compared with higher energy (e.g. 20 kV, Fig. 2). This fact enables the high light-optical magnification at 5 kV. Equipped with a modern light microscope, the field of view is much larger than with a conventional TEM. In addition to the regular film camera, a CCD camera can be attached to the light microscope to provide direct image recording and its further processing with a personal computer.

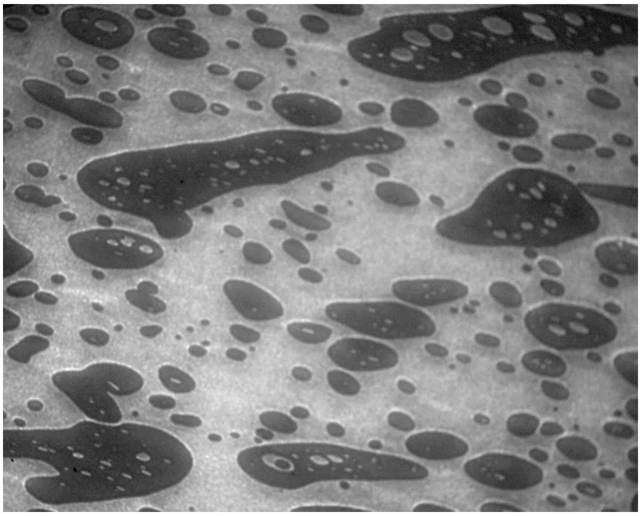

Fig. 3. LV-TEM of polycarbonate/poly(styrene-*co*-acrylonitrile) (50/50) blend. Frame width 6.3 μm. Sectioned with a diamond knife at room temperature; no prior or additional treatment (staining) applied. The dark areas are polycarbonate.

3.2. LV-TEM of polymer blends

3.2.1. Polycarbonate/(styrene-co-acrylonitrile) (PC/SAN)

Phase structure of a PC/SAN blend from stained ultrathin sections was visualised earlier [3,12]. On staining with OsO_4, the polycarbonate appears dark and the SAN remains unstained. In LV-TEM, the PC/SAN blend is visualised with a good resolution and contrast (Fig. 3). As the composition of the PC/SAN 50/50 blend is close to the phase inversion, it is impossible to decide which of the structures corresponds to the PC and which to the SAN. Therefore, blends with a majority of one component were observed. In the PC/SAN 75/25 blend, the majority phase is dark, which means that the dark component corresponds to the polycarbonate (Fig. 4). A consistent result was obtained for the blend with a minority of polycarbonate (PC/SAN 30/70).

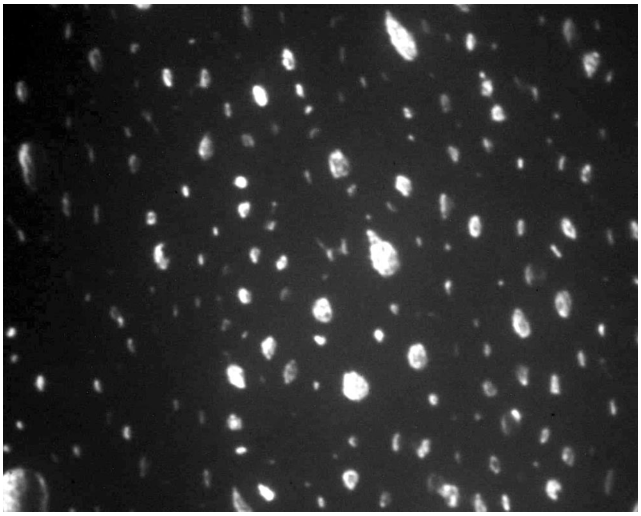

Fig. 4. LV-TEM of polycarbonate/poly(styrene-*co*-acrylonitrile) (75/25) blend. Frame width 6.3 μm. Sectioned with a diamond knife at room temperature; no prior or additional treatment (staining) applied. The dark areas are polycarbonate.

As no additional preparatory treatment (staining) was applied, all the effects observed are to be ascribed to the structure of the materials itself. The basic question arises, what the mechanism of the image contrast is when observing the sample in TEM. Both constituents of the PC/SAN blends are amorphous. Thus, from the point of view of the materials of the sample, there is no crystalline part that would contribute to the image contrast. As far as the elements of the individual constituents are concerned, there are only slight differences, as can be seen from the elemental composition of the monomeric units (Table 1). The SAN component contains a majority of PS; with respect to the styrene/acrylonitrile ratio we can calculate the ratio of the elements C/H/N in the SAN as 28.3/28.3/1. The nitrogen-to-carbon ratio N/C is 0.035. In PC, the ratio of oxygen to carbon is 0.19. For the interaction of the electron beam with the material of the blends, carbon forms a decisive majority of elements. Therefore, there is no reason for different behaviour (scattering) of the electron beam in the blend constituents.

Differences in density of the constituents can be viewed as the only potential source of the image contrast (Table 1). The difference between densities of the components in the PC/SAN sample is 0.13 g/cm^3. The polycarbonate phase, which is of a higher density than the SAN, was observed as dark. To confirm the hypothesis that the density is the factor decisive for the image contrast, we selected other polymer blend systems for observation with the LV-TEM technique.

3.2.2. Polystyrene/polypropylene blends (PS/PP)

Morphology of the blends compatibilized with triblock SBS copolymer CARIFLEX, studied earlier with the common preparation and observation techniques involving staining [13,14], displayed particles of the minority component surrounded by the compatibilizer, the compatibilizer particles being dispersed in either component. Low-voltage TEM of the ultrathin sections yields a similar morphology (Fig. 5). The dispersed particles adhering to the matrix are surrounded by a diffuse layer, which is darker than the particles. Irregular darker areas (probably aggregates of the compatibilizer) are dispersed in the matrix. This kind of morphology is in agreement with the idea that the compatibilizer has a tendency to form regions with its original structure in the vicinity of the interface [14].

3.2.3. Polyethylene/polypropylene blends (PE/PP)

The phase structure of polyethylene/polypropylene blends is difficult to observe, especially from ultrathin sections. Therefore, cut surfaces and/or fracture surfaces techniques are applied, without or with the pre-treatment (cf. Refs. [1,15]). On the other hand, LV-TEM of ultrathin sections provides sufficient contrast to distinguish one

Table 1
Elemental composition and densities of the studied polymers

Polymer	Elemental composition	Density (g/cm^3)
Polystyrene (PS)	C_8H_8	1.04–1.06 (tabulated values)
Polyacrylonitrile (PAN)	C_3H_3N	
Polycarbonate (PC)	$C_{16}H_{14}O_3$	1.20
Low density polyethylene (LDPE)	CH_2	0.915–0.94
PP	C_3H_6	0.90–0.91
Styrene-*co*-acrylonitrile (SAN)	$C_{28.3}H_{28.3}N$	1.07

polymer from the other (Fig. 6). The only difficulty is in preparation of sections of good quality, for which cutting in cryogenic conditions is inevitable and a diamond knife is advantageous.

The minority phase (PP) appears to be lighter than the matrix phase (LDPE, Fig. 6). In this blend, the density differences are much smaller than those in the above blends. As the density of LDPE can be 0.915–0.94 g/cm^3, and the density of PP can exhibit values between 0.89 g/cm^3 (quenched film) and 0.90–0.91 g/cm^3 (slowly cooled film), the density differences between the component can be from 0.005 to 0.04 g/cm^3. The capability of the LV-TEM technique can be seen especially from these polymer blends.

3.3. Low-voltage scanning transmission electron microscopy (LV-STEM)

In order to compare the good results obtained using the LV-TEM technique with scanning transmission observations at low voltages (LV-STEM), the same samples were observed (Figs. 7 and 8) as those that were micrographed with the LV-TEM (Figs. 5 and 6). The accelerating voltage used for the STEM was 25 kV.

The polyethylene/polypropylene blend (Fig. 7) exhibits a good contrast distinguishing the two constituents. Moreover, a fine structure is observed in each of the components. We can speculate that diffraction contrast can contribute to the image contrast, as both components are crystalline.

A compatibilized polystyrene/polypropylene blend observed with the STEM technique (Fig. 8) yields additional information to that obtained with the LV-TEM technique (cf. Fig. 5). More details can be observed in the vicinity of or close to the interface (rings which are probably an interface; small dark dots of an unknown origin, a finer structure in larger particles, which may be the result of the crystalline phase).

3.4. Comparison of the two low-voltage TEM techniques

The most important advantage of both techniques is that no additional treatment of samples is required, i.e. only the material of the sample is present in the specimen. This means that all the features observed have to be taken into account when interpreting the images.

The transmission imaging technique (LV-TEM) is extraordinarily sensitive to the thickness of the specimen (section). Wrinkles of the section (Fig. 6) or undulations

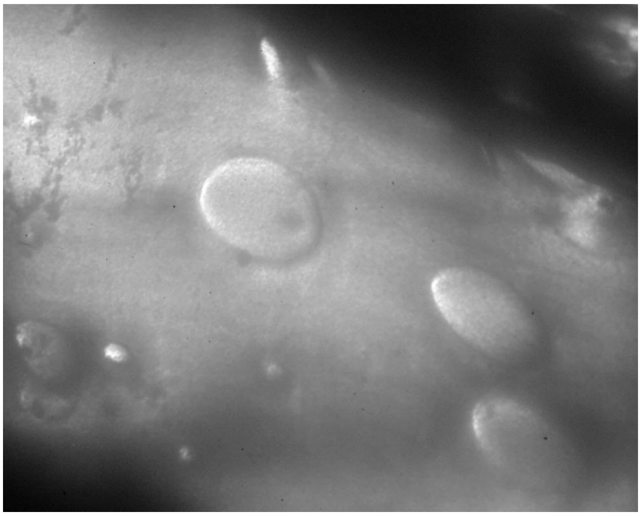

Fig. 5. LV-TEM of polystyrene/polypropylene (80/20) blend. Frame width 6.3 μm. Sectioned with a diamond knife at cryogenic conditions; no prior or additional treatment (staining) applied. The particles are polystyrene, the same object as in Fig. 8.

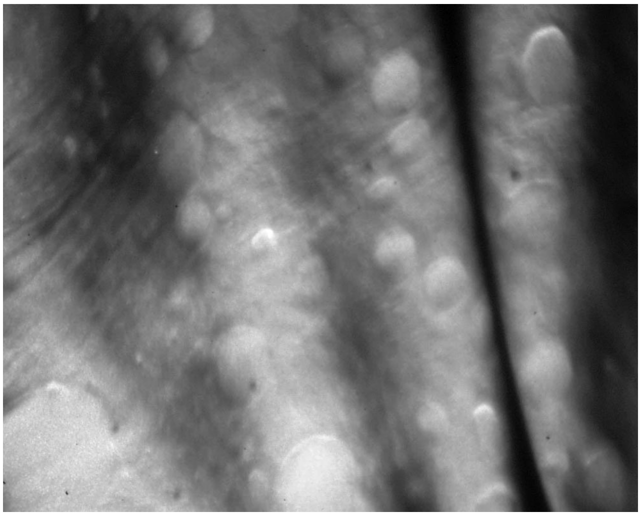

Fig. 6. LV-TEM of low-density polyethylene/polypropylene (80/20) blend. Frame width 6.3 μm. Sectioned with a diamond knife at cryogenic conditions; no prior or additional treatment (staining) applied. The particles are polypropylene.

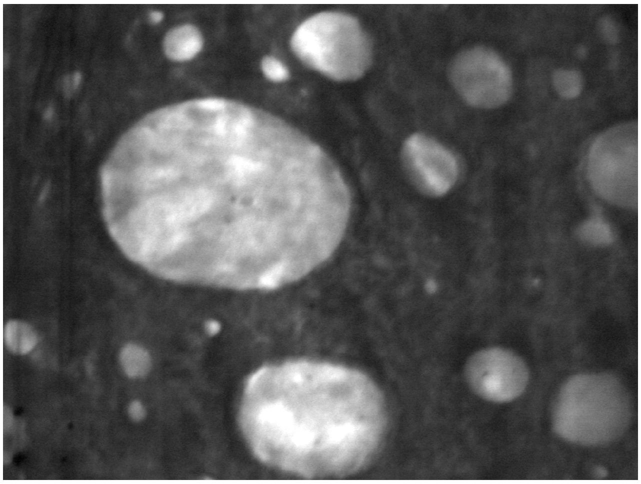

Fig. 7. LV-STEM of low-density polyethylene/polypropylene (80/20) blend. Frame width 9.7 μm. Sectioned with a diamond knife at cryogenic conditions; no prior or additional treatment (staining) applied. The particles are polypropylene.

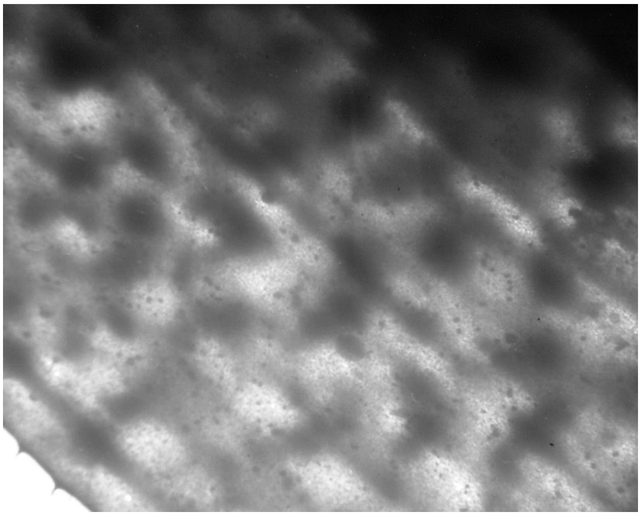

Fig. 9. LV-TEM polypropylene blend ADFLEX. Frame width 6.3 μm. Sectioned with a diamond knife at cryogenic conditions; no prior or additional treatment (staining) applied.

in the section thickness (chatter) can be very critical. Images of sufficiently thin amorphous specimens can reveal further details. The phase structure in the PC/SAN blends obtained with LV-TEM was compared with that observed in conventional TEM after staining. While staining displays some zones between the PC and SAN components [12], LV-TEM reveals that transitional regions exist between the two regions (Fig. 3), in which a concentration gradient of either of the components can be observed with the technique used. A detailed study of the effects is in progress.

The different sensitivities of the two methods to various material parameters can be compared from Figs. 9 and 10, and Figs. 6 and 7. Differences in local density of the specimen observed with LV-TEM (larger dark spots in Fig. 9) are not so well seen when observed with LV-STEM (Fig. 10), while smaller dark dots which are probably from a different material can be observed with both techniques. The finer structure in crystallizable polyolefins (polyethylene, polypropylene), which was observed with STEM (Fig. 7), could not be observed with LV-TEM (Fig. 6).

Radiation damage is an inherent parameter of any electron microscopy technique. It can be expected that the two techniques discussed here differ in that parameter as well. Presumably the scanning transmission technique (LV-STEM) will damage susceptible specimens to a higher extent than the TEM technique. Experiments are in progress to compare the radiation damage of crystalline polymers.

It is not easy to prepare electron microscopy specimens which are sufficiently thin. Even using diamond knives,

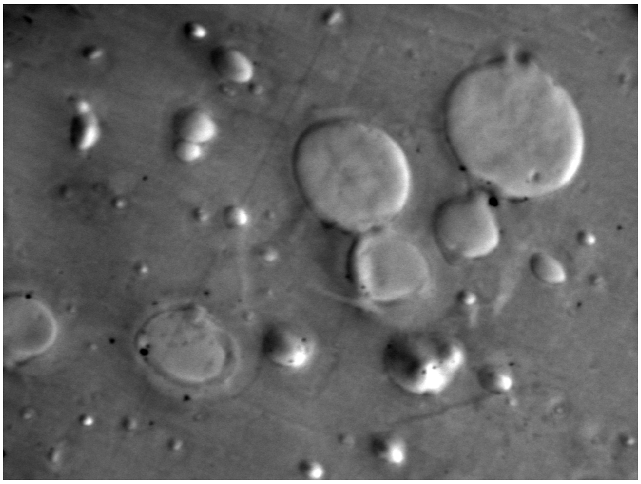

Fig. 8. LV-STEM of polystyrene/polypropylene (80/20) blend. Frame width 12.9 μm. Sectioned with a diamond knife at cryogenic conditions; no prior or additional treatment (staining) applied. The particles are polystyrene, the same object as in Fig. 5.

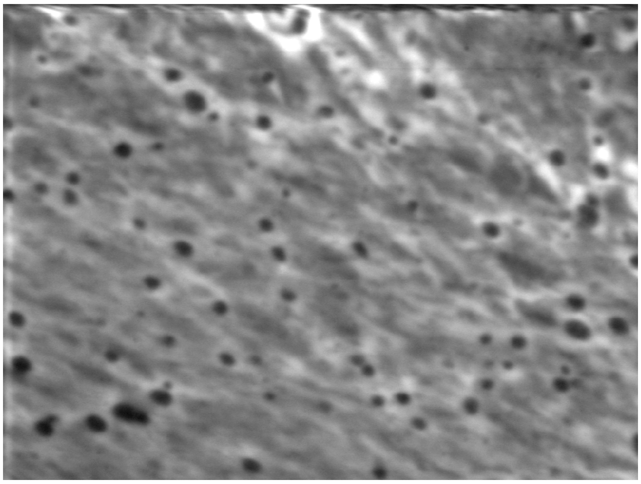

Fig. 10. LV-STEM polypropylene blend ADFLEX. Frame width 9.7 μm. Sectioned with a diamond knife at cryogenic conditions; no prior or additional treatment (staining) applied.

ultrathin sectioning is more difficult in cryo-conditions. Sections obtained at room temperature (PC/SAN) are usually more uniform and not undulated, unlike those which must be prepared in cryo-conditions (polyolefin-containing materials). In the case that the specimens are too thick to be observed with the LV-TEM technique, LV-STEM can be a possible solution. A compromise must be sought between radiation damage, specimen thickness and the information, which can be obtained.

The mechanisms of the imaging contrast are not fully understood yet. However, it can be stated that the two techniques are rather complementary and that the differences in imaging the same systems probably refer to different structure parameters.

4. Conclusions

The morphology of polymer blends can be visualised from thin films (sections) without any further pre-treatment (staining) if low-voltage electron microscopy techniques (LV-TEM, LV-STEM) are used.

With the techniques, it is possible to distinguish components differing very slightly in their elemental compositions.

The difference in density between the individual components of polymer blends was found to be the reason for obtaining a sufficient image contrast. Differences less than 0.04 g/cm^3 were sufficient to identify the phase structure.

The two techniques referred to are rather complementary. Each of them yields slightly different images of the same objects. The mechanism of imaging is not fully understood yet and it is the object of further studies.

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References

[1] Vesely D. Practical techniques for studying blend microstructure. In: Folkes MJ, Hope PS, editors. Polymer blends and alloys, London: Blackie, 1993. p. 103–25.
[2] Lednický F, Pelzbauer Z. Polym Test 1987; 7:91–107.
[3] Hromádková J, Lednický F, Kolařík J. Polym Test 1994;13:461–78.
[4] Lednický F, Hromádková J, Kolařík J. Polym Test 1992;11:205–13.
[5] Gedde UW. Polymer physics, London: Chapman & Hall, 1995.
[6] Kolařík J, Lednický F, Pegoraro M. Polym Networks Blends 1993;3:147–54.
[7] Kolařík J, Lednický F, Locati G, Fambri L. Polym Engng Sci 1997;37:128–37.
[8] Hlavatá D, Horák Z, Lednický F, Tuzar Z. Polym Networks Blends 1997;7:195–202.
[9] Kruliš Z, Horák Z, Lednický F, Pospíšil J, Sufcák M. Angew Makromol Chem 1998;258:63–68.
[10] Delong A. Low voltage TEM. Elect Microsc 1992.
[11] Delong A, Hladil K, Kolařík V. A low voltage transmission electron microscope. Eur Microsc Anal 1994;27:13–15.
[12] Lednický F, Hromádková J, Kolařík J. Polym Test 1999;18:123–4.
[13] Hlavatá D, Horák Z, Lednický F, Pleska A. Compatibilization efficiency of S–B multiblock copolymers in PS–PP blends. EURADH'98—WCARP-1, 4th European Conference on Adhesion, First World Congress on Adhesion and Related Phenomena, 6.–11.9.1998, Garmisch-Partenkirchen, Abstracts 2.33. In preparation.
[14] Lednický F, Horák Z, Hlavatá D, Hromádková J. Polystyrene/polypropylene blends: morphology of their compatibilizers and of the interphase. European Conference on Macromolecular Physics Morphology and Micromechanics of Polymers, Merseburg 27.9.–1.10.1998. Pick R, editor. EPS Abstracts. Vol. 22I, PI-19, p. 152.
[15] Bonner JG, Hope PS. Compatibilisation and reactive blending. In: Folkes MJ, Hope PS, editors. Polymer blends and alloys, London: Blackie, 1993. p. 46–74.