JOURNAL OF MATERIALS SCIENCE 26 (1991) 6357–6361

Influence of the electric field on the microscopic structure of PEO/PMMA blends

T. STERZYNSKI*, J. GARBARCZYK
Technical University of Poznań, Lab. for Polymers, PL 60-965 Poznań, Poland

Binary blends of semicrystalline poly(ethylene oxide) (PEO) with amorphous poly(methylmethacrylate) (PMMA) were investigated during isothermal crystallization (without and with application of electric field) with respect to the segregation behaviour of the spherulitical structure. Microscopic investigations of the blends crystallized without electric field, confirmed earlier results that below 50 wt% PMMA the amorphous domains are distributed in the crystalline phase. The electrocrystallization of the blends in the presence of a strong electric field caused an important increase in nucleating density and formed PEO spherulites with near circular shape, as explained using the bursting theory of Garton and Krasucki.

1. Introduction

New properties of materials may be achieved by mixing two or more semicrystalline as well as amorphous polymers. The mixture of polymers may change the macromolecular structure. In the case of semicrystalline polymers, qualitative and quantitative changes in the spherulitic structure may occur. Many investigations exploring this phenomenon have been reported. Martuscelli *et al.* [1] studied the polymer blend consisting of semicrystalline poly(ethylene oxide) (PEO) and amorphous poly(methylmethacrylate) (PMMA). They analysed the morphology of thin films obtained by solution casting by crystallization of the PEO in an amorphous PMMA matrix and determined the increase of the nucleation density as a function of the increasing PMMA content. In blends containing less than 50 wt % PMMA, they found that amorphous domains were distributed between crystalline ones, and therefore are not observable by polarized light microscopy [1, 2].

It is well known that besides the effects of mixing, the modification of the polymer structure may be caused by physical agents such as electric field, radiation or pressure fields. Bagirov *et al.* [3] studied the influence of electric charges in air on the crystallinity of polymer dielectrics and found that the degree of crystallinity of certain polymers depends on the amount of electric charge.

In our earlier work on the influence of an electric field on the crystalline structure of low-density poly(ethylene) (PELD) it was shown that the electric field caused changes in the dimensions of the elementary cell as well as in the orientation of macromolecular chains [4].

The effect of the electric field on the morphology of crystalline PEO and amorphous polystyrene (PS) blends was investigated by Moriya *et al.* [5] among others. They observed that the spherical domains of PEO in the polystyrene matrix under the electric field break into smaller spheroids and are oriented towards the direction of the field.

Undesirable changes in the properties may be caused as a result of applying an electric field. Extended exposure may be used as an ageing agent. This may be especially important in such electronic or electromechanical applications where, for example, high-voltage electric lines or/and insulating materials are persistently exposed to the influence of a strong electric field. The resultant changes in mechanical and physical properties could be caused not only by natural thermo-oxidation but also by the electric field.

In the present work we studied the morphology of PEO–PMMA blends and the influence of electric field on the morphology of the PEO–PMMA blends, particularly on the distribution of the PEO spherulites during the electrocrystallization in the amorphous PMMA matrix.

2. Experimental procedure

2.1. Material

The poly(ethylene oxide) was PEO 35 000 (Hoechst) and the poly(methylmethacrylate) was PMMA 8A (Rohm). The homopolymers, as well as binary blends, were dissolved in trichloromethane ($CHCl_3$) in the volumetric proportion of 1 part polymer to 7 parts solvent. After mixing for 5 h, the solutions were paned on microscopic slides and dried in air for about 24 h. To ensure the complete removal of the solvent, the samples were kept in a vacuum for 22 h at 333 K.

---

* *Present address*: Ecole d'Application des Hauts Polymeres, F-67000 Strasbourg, France.

0022–2461/91 $03.00 + .12

Final cooling was also done in a vacuum. The resultant samples were in the form of thin plates with a thickness about 10 μm.

Binary blends containing the following weight percentages of PMMA in PEO were prepared: 10%, 30%, 50%, 90%.

2.2. Electropolarization

The PEO–PMMA blends were put in a device as shown in Fig. 1. To exclude the thermo-oxidation of molten polymer blends, the cell, laden with samples was evacuated to 10^{-7} torr, (1 torr = 133.322 Pa) filled with nitrogen and similarly evacuated. The electric field was applied after the melting temperature (343 K) was reached and continued until cooling to the ambient temperature. Fast cooling of the PEO–PMMA blends was done using liquid nitrogen flowing through the cooling channels of the device.

The application of the electric field and the control of the temperature as functions of time are presented in Fig. 2.

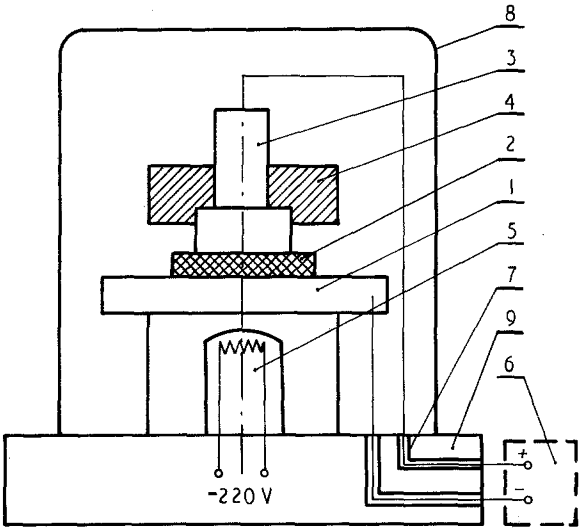

Figure 1 The electropolarization apparatus: 1 electrode with oven; 2, sample; 3, upper electrode; 4, electrode handle; 5, heater; 6, high current supply; 7, handle and isolation; 8, glass cover; 9, base plate.

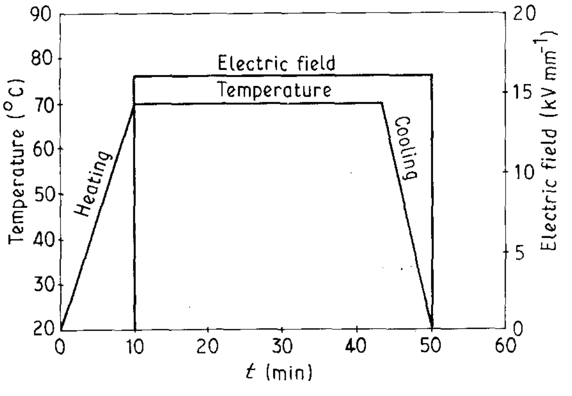

Figure 2 The run of the temperature, *T*, and the electric field, *E*, during the electropolarization as a function of time.

2.3. Structure investigations

The investigations to determine the structure were done using a Leitz microscope with a polarization unit and a camera attached to the occular. The results were compared with samples which were crystallized without the application of the electric field.

3. Results and discussion

3.1. The morphology of PEO–PMMA blends as-cast with different amounts of PMMA

Poly(ethylene oxide) [6, 7] crystallizes from a solution in the form of spherulites which are characterized by a Maltese cross structure. For cast films of PEO, crystallized from $CHCl_3$ solution, spherulites with a clear nucleation centre and a clear direction of growth were observed (Fig. 3). The borders between the spherulites are straight lines. This indicated an athermal type of growth, which was also observed by Martuscelli *et al.* [1]. There are two explanations of the phenomenon of straight-line borders.

1. The nucleation of all of the spherulites may take place simultaneously, e.g. at the same time after forming a film from solution.

2. The growth rate of the lamellae forming the spherulites is constant and equal for all directions of growth.

It was not possible to distinguish between either phenomenon for the film studied in this report. During experiments, necessary conditions were ensured to achieve crystallization with a regular distribution of PEO in solvent and a constant temperature during crystallization.

The mixture of PEO and PMMA consisted of crystalline and amorphous domains of PEO as well as amorphous domains of PMMA. The influence of amorphous domains of PMMA on the crystalline structure of PEO is shown in Figs 4–6. For a low amount of PMMA (Fig. 4) mixed with PEO, no amorphous domains between, or in, the spherulites were observed. However, for PEO/PMMA blends of 50/50 small black amorphous domains were situated between the spherulites (Fig. 5).

These observations were in very good agreement with data reported by Martuscelli *et al.* [1]. In Fig. 6,

Figure 3 The spherulites of pure PEO cast from solution; the diagonal of the picture is 0.550 mm.

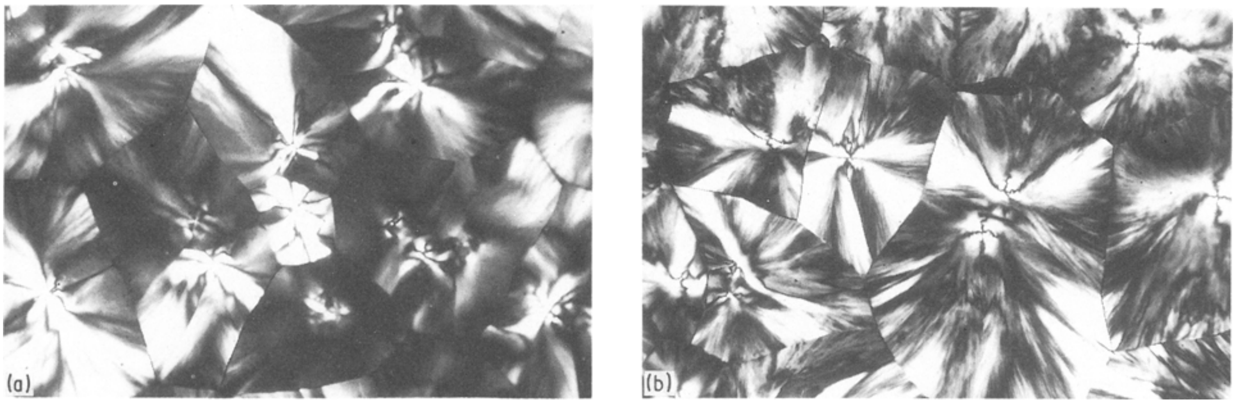

Figure 4 The PEO/PMMA blend cast from solution; the diagonal of the picture is 0.550 mm: (a) 10 wt % PMMA; (b) 30 wt % PMMA.

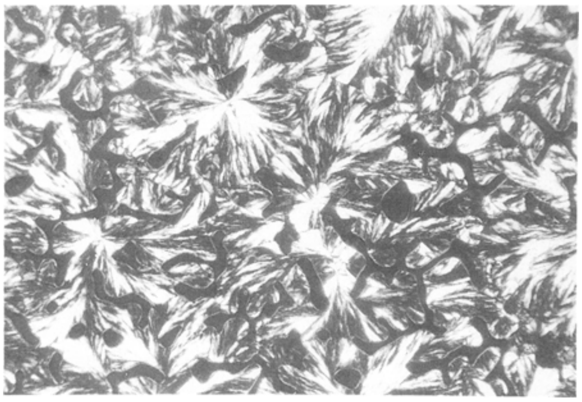

Figure 5 The PEO/PMMA blend cast from solution; the diagonal of the picture is 0.550 mm; 50 wt % PMMA.

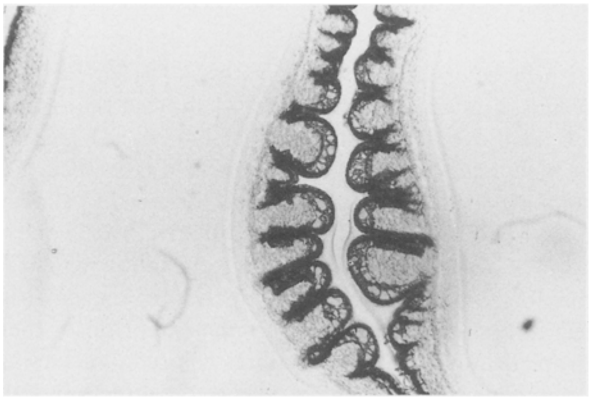

Figure 6 The PEO/PMMA blend cast from solution; the diagonal of the picture is 0.550 mm; 90 wt % PMMA.

blends consisting of 90 wt % PMMA had large amorphous areas with small spherulites. These spherulites are nucleated on the borders of the amorphous domains. This indicated significant demixing of the mixture.

This phenomenon may be explained in the following manner. The presence of PMMA, even in small quantities, in the PEO solution causes irregularity in the boundaries between spherulites and an irregular growth of lamellae. As a consequence, non-simultaneous nucleation takes place as well as an uneven growth rate of the lamellae in different directions from the centre of the spherulites. However, the following alternative mechanisms were also possible.

(a) simultaneous nucleation of spherulites with an unequal growth rate for different spherulites;

(b) non-simultaneous nucleation with an unequal growth rate for all domains;

(c) nucleation taking place at different times with growth rate of the lamellae varying from one crystal domain to the other as well as in several spherulites. On the basis of the literature data the most likely mechanism was (c).

3.2. The influence of the strong constant electric field on the spherulitical structure of PEO/PMMA blends

The electric field was applied to the cast films of PEO and PEO/PMMA blends at the conditions described above. The temperature of 343 K was higher than the melting temperature of the PEO crystals. Therefore, only amorphous domains existed at the start of the experiments and during cooling the crystallization of PEO from the melt in the electric field took place.

For comparison, crystallization of films of pure PEO was carried out (Fig. 7). A significant change in the shape and dimensions of the PEO spherulites resulted. The diameter of the spherulites was smaller by several factors and the borders were almost perfectly circular spherulites, as opposed to the straight ones noted before. In Fig. 8 the significant border-line between PEO spherulites crystallized in the same time–temperature conditions, but without and with electric field, is presented. For the spherulites grown without the electric field no important changes relative to the spherulites of Fig. 3 were noted.

For the mixtures of PEO and PMMA, the same influence of electric field on the kinetics of nucleation and of the growth of PEO spherulites was observed. A strong electric field (with an energy between 12 and $18\,\mathrm{kV\,mm^{-1}}$) caused an increase in the nucleating density of PEO and limited the growth of the spherulites. This limitation applied not only to the dimensions, but also the shape; similar to the PEO films, spherulites with nearly exact circular shape were observed (Figs 9 and 10).

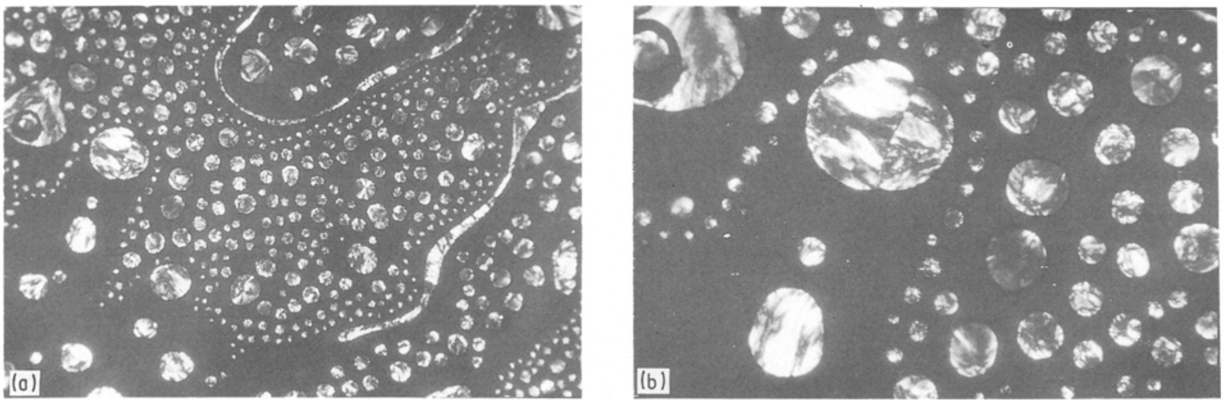

Figure 7 The spherulites of pure PEO cast from solution exposed to an electric field of $E = 12\ \mathrm{kV\,mm^{-1}}$. (a) The diagonal of the picture 2.20 mm, (b) the diagonal of the picture 0.880 mm.

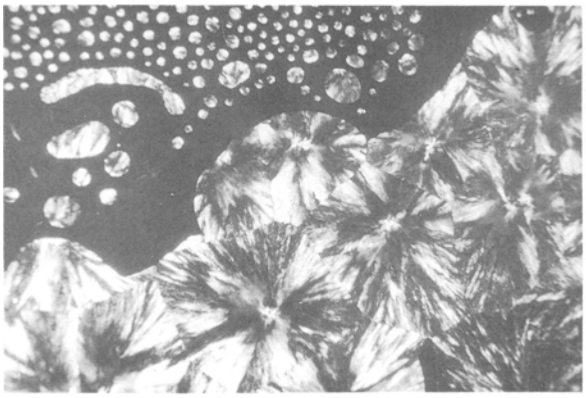

Figure 8 Border-line between spherulites of pure PEO crystallized under the same thermal conditions, but with electric field, E, and without an electric field; the diagonal of the picture 2.20 mm.

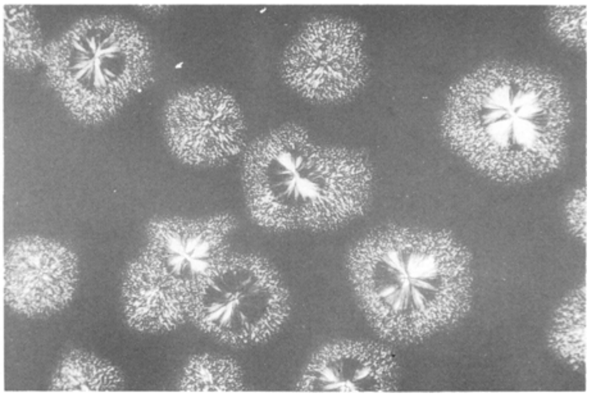

Figure 10 PEO/PMMA blend with 50 wt % PMMA exposed to an electric field $E = 18\ \mathrm{kV\,mm^{-1}}$; the diagonal of the picture 0.690 mm.

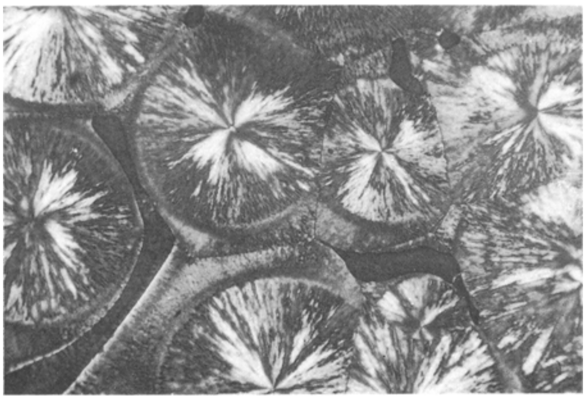

Figure 9 PEO/PMMA blend with 30 wt % PMMA exposed to an electric field $E = 18\ \mathrm{kV\,mm^{-1}}$; the diagonal of the picture 0.690 mm.

It is well known that mechanical and optical properties of polymers depend on the size and shape of the spherulites. Therefore, by varying the strength of the electric field as well as the interaction of both domains (amorphous and crystalline), materials may be obtained with different spherulitic structures and therefore with enhanced mechanical and optical properties.

The above observations were in good agreement with those obtained by Moriya *et al.* [5] for PEO/PS blends. Garton and Krasucki [8] showed that spheriodal oil droplets in a low molecular liquid medium become unstable when an electric field is applied. The similarity between our results and those in [5] allowed us to apply the Garton and Krasucki's theory, on the basis of which (the bursting effect) the following effects may be explained. (1) The dissipation of bigger droplets into smaller ones, and (2) the extension of these droplets into long and thin fibres whose main axes are oriented in the direction parallel to the direction of the electric field.

Because, in our case, the electric field caused the occurrence of a great number of small spherulites (Fig. 7–10), it allowed us to assume that the molten crystal domains of PEO could be treated as droplets distributed in amorphous domains of PMMA. On the basis of the bursting theory and the investigation of Garton and Krasucki [8], the melted PEO-crystal domains, which have a lower viscosity than the viscosity of the amorphous matrix (PEO and PMMA), form spherical droplets, which are dissipated and elongated under the influence of an electric field.

A better knowledge of the physical changes of the spherulitic structure of amorphous/crystalline polymer blends may be practically applied to obtain materials with defined mechanical and optical properties, and to prevent possible undesirable changes in structure and properties of the polymer blends, which are exposed for a long time to a strong electric field. Although the experiments described in this paper were performed at elevated temperatures, the long-term influence of the electric field at ambient temperatures should also lead to comparable changes of the structure of several polymers. To prove the occurrence of the bursting effect in polymer blends, further experimental research needs to be done.

4. Conclusions

1. An electric field applied to PEO and PEO/PMMA in a molten state and during crystallization caused an increase of the nucleating density of PEO spherulites.

2. Similar to the bursting effect, the electric field may create a dissipation of bigger droplets of molten PEO into smaller ones with a spherical shape, and subsequently a growth of PEO spherulites which retained this shape.

Acknowledgements

The financial support of the Polish Academy of Science, (project CPBP 01.12) is greatly acknowledged. Part of the work was done at the Philipps University of Marburg, (FRG), supported by the Alexander von Humboldt Foundation. The authors thank Professor Dr W. Ruland for his suggestions and detailed discussions.

References

1. E. MARTUSCELLI, *Makromol. Chem.* **187** (1986) 1557.
2. A. E. WOODWARD, "Atlas of Polymer Morphology" (Carl Hanser Verlag, München, 1988) p. 310.
3. M. A. BAGIROV, *Wysokomolekularnyje Sojedinienia* (*A*) **XXIX** (1987) 917.
4. T. STERZYNSKI, in "Interpretation of Fundamental Polymer Science and Technology-2", edited by P. J. Lemstra (Elsevier Applied Science, Essex, 1988) p. 436.
5. SATORU MORIYA, KEIICHIRO ADACHI and TADAO KOTAKA, *Polymer Commun.* **26** (1985) 235.
6. M. PRACELLA, *Eur. Polym. J.* **21** (1985) 551.
7. T. SHIMADA, *Makromol. Chem.* **181** (1980) 2043.
8. C. G. GARTON and Z. KRASUCKI, *Proc. R. Soc.* **280A** (1964) 211.

Received 30 May 1990
and accepted 18 March 1991