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Improvement of the dispersion degree in incompatible polystyrene/poly(*n*-butylmethacrylate) blends by the graft poly(2,6-dimethyl-1,4-phenylene oxide) on poly(*n*-butylmethacrylate)

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SUMMARY

Using optical and electron microscopy it is evidenced that the introduction of graft copolymer poly(2,6-dimethyl-1,4-phenylene oxide) on poly(n-butylmethacrylate) improves substantially the degree of dispersion in the incompatible polymer blend polystyrene/poly(n-butylmethacrylate). The action of the copolymer is attributed-besides the mutual dissolution of the PBMA sequences - to the compatiblity between the PPO-grafts and the PS component of the blend. This is supported by the Tg data which show that the Tg of the PS in the blend is influenced by the present graft copolymer. The observed decrease of the Tg is explained by the concomitant admittance in the PS phase of the PBMA backbone together with the PPO grafts.

INTRODUCTION

Among the divers possibilities of production of new polymeric materials, the realization of polymer blends has gained an increased attention in the last decades. The often used synonym of "polymer alloys" suggests that polymer blends may exhibit new characteristic properties.

There are known two basically types of polymer blends. Blends of compatible components, i.e. of miscible polymers and blends of incompatible components. The latter are two or multiphase systems and are the more important ones from the technical point of view(1).

In the two phase systems the component present in minor concentration is dipersed in the "matrix" of the second component and both the morphologic stability and the mechanic properties depend essentially on the adhesion between the components.

Several ways are used to stabilize two or multiphase sytems; one of the ways uses blockcopolymers or grafted copolymers to improve the adhesion between the incompatible components of the blend(2). Generally it is assumed that blockcopolymers are superior and that the efficiency of adhesion increases with the length of the blocks(3).

Nevertheless, in the present paper are analyzed the adhesion effects of grafted copolymers of poly(2,6-dimethyl-1,4-phenylene oxyde) - PPO - in poly(n-butylmethacrylate) - PBMA - backbone, g-PPO-co-PBMA - on the incompatible polystyrene/poly(n-butylmethacrylate) - PS/PBMA - blend, taking into account the well known compatiblity of PS and PPO. The grafted copoplymers were synthesized by Percec et al.(4)

The PS/PBMA system is a typical incompatible polymer mixture(5). Lipatov et al. have shown that the incompatibility decreases with increasing temperature(6). The interaction parameter shows a minimum value in blends with 20-40 w/w % PBMA(7). The compatibilizer effect of PS-PBMA copolymers has been investigated by Fujioka et al.(8) A comparison of the theoretical predictions concerning miscibility and experimental results is presented in the paper of Somani and Shaw(9).

EXPERIMENTAL

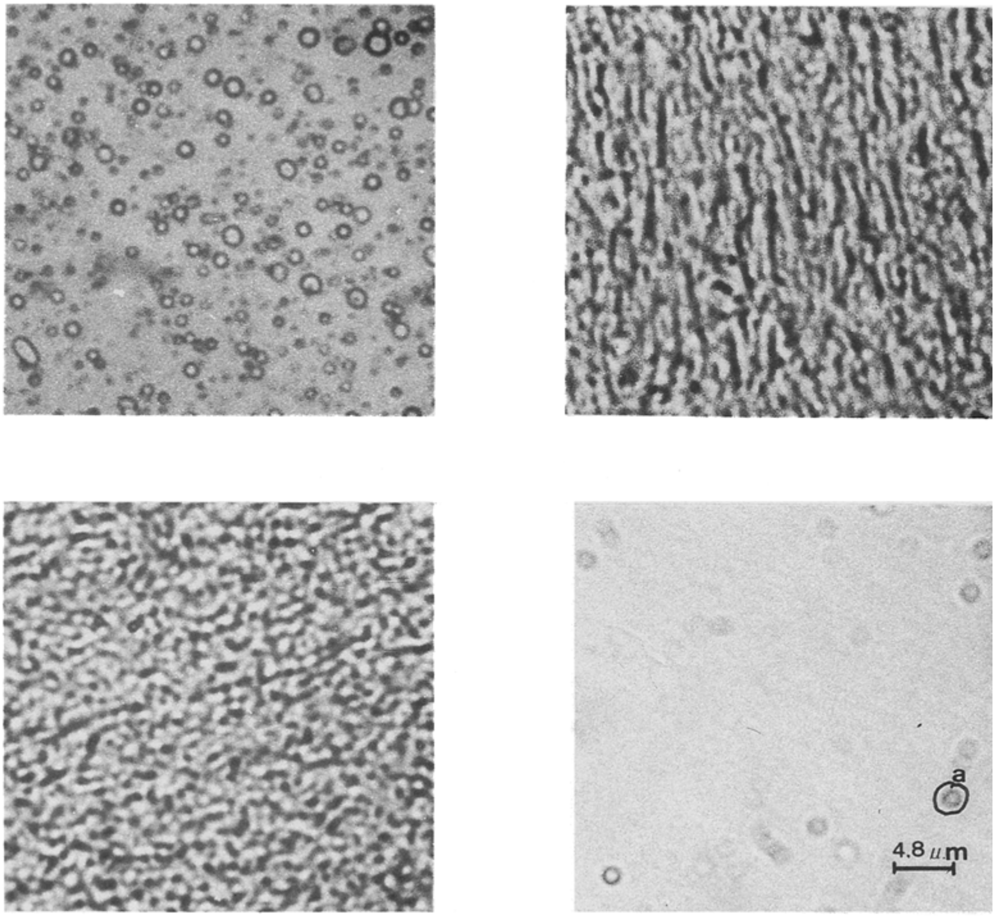
The following components were used for blend preparation by dissolution in benzene and freeze-drying in vacuum at -70° C.
Atactic polystyrene - PS - (of BASF), M_w=63,000 and M_w/M_n=2.55 (by GPC)
Atactic poly(n-butylmethacrylate) - PBMA - (of Röhm), M_w=193,000 and M_w/M_n=1,6 (by GPC)
Compatibilizer agent: g-PPO-co-PBMA, M_w=166,000, 5 grafts/molec., M_{graft}=2,600. The graft copolymer was purified by dissolution at 60° C in chloroform and reprecipitation with methanol/toluene (4:1).

There were prepared four blends containing respective 0, 10, 20 and 30 mole% of g-PPO-co-PBMA. In all blends were maintained constant the contents of PBMA (30 mole%) and of PS (70 mole%). The respective PPO and PBMA contents of the compatibilizer introduced in the blends were accounted for the needed PS and PBMA for blend preparation. After freeze-drying the blends were further dried in vacuum at 100° C until constant weight.

The blends were investigated by optical methods (microscopy and electron-microscopy), DSC and small angle light scattering. The thermal stability of the temeparture sensitive PBMA was proved by thermogravimetry in air and argon, respectively, at the heating rate of 2K/min, using the Netzsch STA 429 thermobalance. Degradation in air started at 210° C and in argon at 247° C.

RESULTS and DISCUSSION

By simple visual observation the blends showed a graduate increase in transparency with increasing content of the compatibilizer graft copolymer. Whereas the initial PS/PBMA blend without compatibilizer was turbid, the blend with 30% copatibilizer was in fact translucent. This visual observation of increased improvement of the dispersion degree in the PS/PBMA system was confirmed by the microscopic investigation (magnification of 320) as evidenced by the photographs shown in Fig. 1. The films of 0.2 mm thicknes were squeezed between two quartz plates and then controlled heated to 190°C and recooled to 50°C. Subsequently the microscopic photographs were taken.

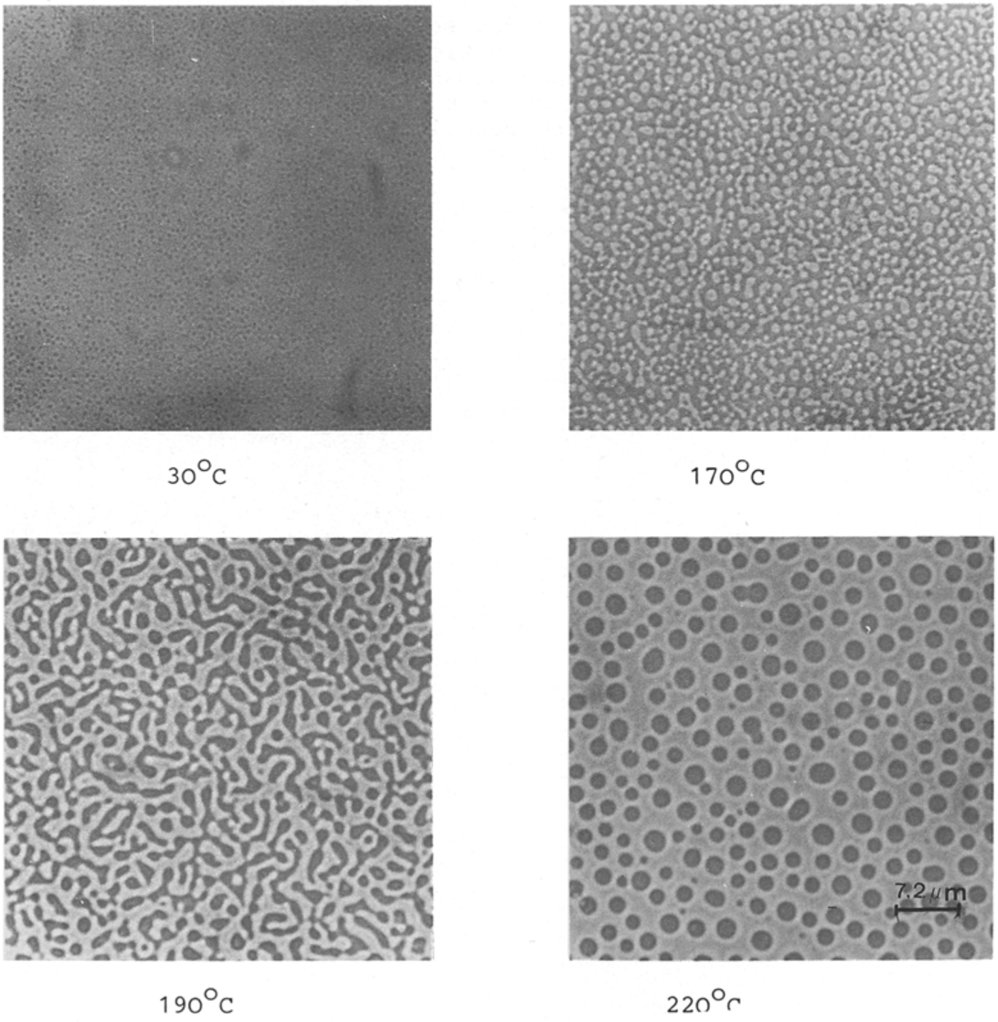


20 %

30 %

Fig. 1 Microphotographs of the PS/PBMA Blend without and with graft copolymer g-PPO-co-PBMA. a. Dust particles

In a second set of microscopic investigation solution casted films were slowly heated starting from room temperature. The temperature of starting phase separation characterized by the fusion of the dispersed particles was adopted as a criterion of the compatibilizing effect of the introduced graft copolymer.



30°C

170°C

190°C

220°C

Fig. 2 Temperature Induced Confluence of the Dispersed PBMA Particles in the Incompatible PS/PBMA Blend without Graft Copolymer

In Fig. 2 are shown the respective pictures of the PS/PBMA blend without compatibilizing graft copolymer. Accordingly to the above definition the characteristic phase separation temperature was considered to be of about 170-190°C. In the blends with graft copolymer the respective temperatures were of about 250-260° for the blend with 10% copolymer, 280-290° for that with 20% copolymer and 270-280°C for the blend with 30% copolymer.

The optical investigation of the studied PS/PBMA blends was continued by elecetron microscopy, using the "Zeiss CEM 902" with an attached elcetron-energy loss spectrometer. The micrographs were judged by using the computer-assisted grey-value evaluation system IBAS 2000. Two series of blend samples were investigated. The samples of series A were annealed for 1/2 h at 170°C, those of series B were annealed for 1 h at 190°C. The sample films were obtained by vacuum-assisted compression-moulding using a pressure of 20Kg/cm². Subsequently cuts of 100 nm thickness were cutted by using the Reichert-Jung ultramicroton "Ultracut E". All samples were investigated using the magnification of 3,000 and 20,000 fold, respectively.

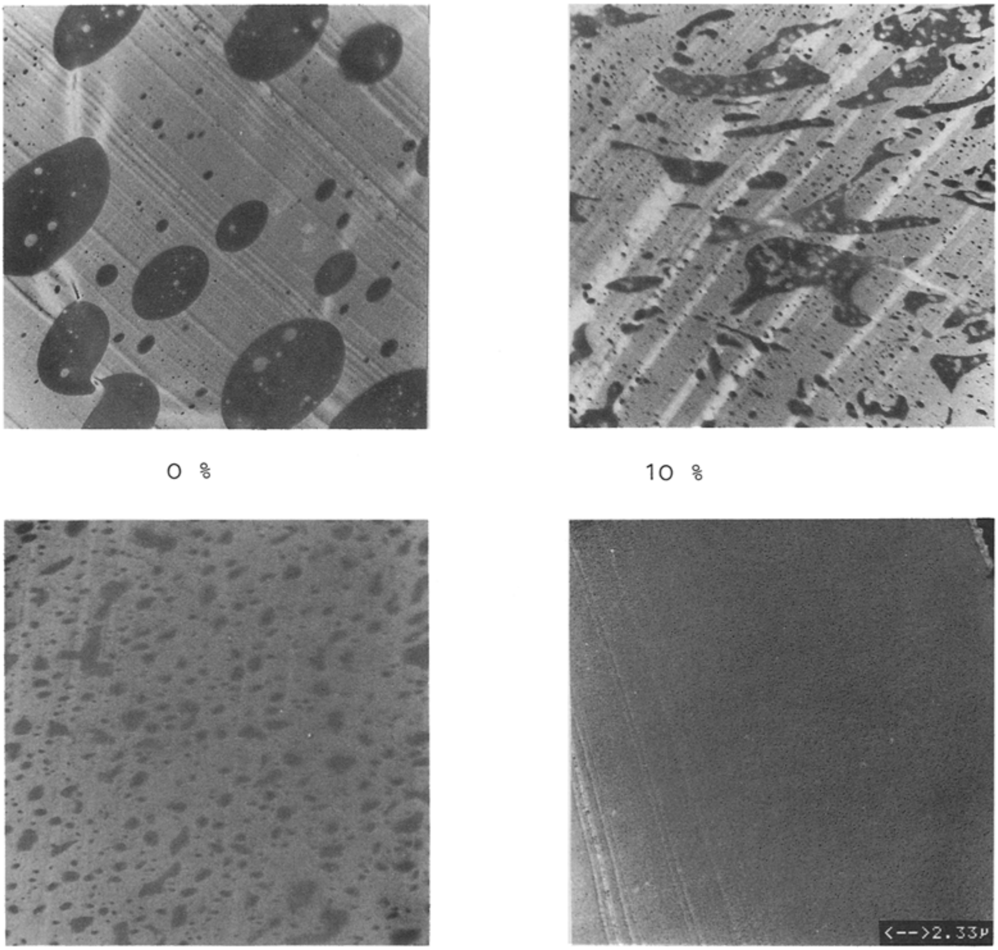
Taking into account the destruction of methacrylates by electron beams, the contrast of the samples was realized by degradation of the PBMA in the electron beam of 80 KeV. In a subsequent 60 eV energy loss beam the dispersed PBMA appears dark in the light PS matrix.

Representative electron-micrographs of the blends of series B, obtained with the magnification 3,000 are presented in Fig.3. The matrix inversion shown by both blends without and with 10% graft copolymer was also observed in the micrographs of series A.

The maximal diameter of the dispersed PBMA particles was in the blend without copolymer of 7 μm and in the blend with 20% copolymer of about 1 μm. The irregular shape of the PBMA domains in the blend with 10% copolymer excluded the evaluation of a typical domain diameter. The particle diameter in the blend with 30% copolymer was found to be of about 0.1 μm, by using the micrographs obtained with the 20,000 fold magnification.

The computer-assisted grey-value evaluation of the micrographs was possible only for the blends with 0, 10 and 20% graft copolymer, respectively. Both, the particle size and the contrast were to small in the blends with 30% copolymer to be used for computer-assisted grey value evaluation.

The obtained results are presented in Table 1. There are included the Tg data obtained by using the PERKIN-ELMER DSC 7. The given Tg values are the midpoint temperatures extrapolated for zero heating rate.



0 %

10 %

20 %

30 %

Fig. 3 Electron Microscopic Pictures of the PS/PBMA Blend without and with Graft Copolymer g-PPO-co-PBMA (Micrographs of the blends of series B at the electron energy loss of 60 eV)

Table 1. Characteristics of the PS/PBMA Blends (Global content of PBMA 30 mole%)

Blend	PS/PBMA	10% of g-PPO-co-PBMA	20% of g-PPO-co-PBMA	30% of g-PPO-co-PBMA
Tg_{PBMA}, °C	22.9	19.5	22.0	22.3
Tg_{PS}, °C	97.2	97.0	92.1	91.3
Mean surface of PBMA-Domains (%)	26.17±3.51	20.61±6.73	13.82±4.66	-
Mean correlation length (μm)	1.98±0.51	0.33±0.07	0.32±0.10	-

The decrease of the mean correlation length in the blends with compatibilizing graft copolymer confirms the decrease of the size of the PBMA-particles in the PS matrix, i.e. the increase of the degree of dispersion in the PS/PBMA blends with increasing content of the graft copolymer. This decrease in size of the dispersed PBMA particles is accompanied by an increase of the share of the interphase contour. This affects the counted surface of the dispersed particles and explains therefore the apparent decrease of the PBMA content expressed by the mean surface of the PBMA domains.

Concerning the DSC data it is interesting to notice that the Tg of the PPO sequences could not be observed in DSC, even in the pure graft copolymer g-PPO-co-PBMA. Accordingly to literature the PPO of the molecular weight of that of the PPO grafts should be of about 160°C(10). The absence of the PPO Tg in these grafted copolymers was also remarked by Mühlbach et al.(11), who showed that the Tg of PPO is evidenced by DSC only for PPO grafts of a molecular weight higher than 7,000. The Tg of the blend components PS and PBMA are in the blend without copolymer identical with the values reported in literature for the pure homopolymers(12).

It is remarkable that in the blends with the grafted copolymers the Tg of the PBMA is not affected by the introduction of the copolymer g-PPO-co-PBMA, whereas the Tg of the PS decreases suggesting the influence of the disolved compatible PPO grafts in the PS matrix. Due to the fact that the PBMA chains of the copolymer are addmitted simultanousely in the PS matrix, the decrease of the Tg of the PS seems explicable.

Although small angle light scattering data suggest an evident difference between the behaviour of the blend without grafted copolymer and of those with grafted copolymer, mainly with 30 mole% of g-PPO-co-PBMA, the large scatter of the data and the inherent difficulties encountered in an accurate separation of the scattered and the reflected light intensities prevented the evaluation of quantitative values.

In conclusion all experimental data suggest effective adhesion action of the grafted PPO-co-PBMA copolymer in the incompatible PS/PBMA blends, although the molecular weight of the PPO grafts compatible with the PS is far below the molecular weight of the PS matrix. With increasing content of the copolymer the dispersion degree of the PBMA in the PS matrix increases substantially. The simultaneous decrease of the Tg of the PS matrix due to the presence of the graft copolymer suggests the admission of the compatible PPO grafts in the PS matrix. The decrease of the Tg could be the result of the concomitant admittance of the PBMA-backbone which contains the PPO grafts.

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