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Low frequency viscosities of PS/PMMA/PS-b-PMMA blends

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Abstract

Assuming that the viscosimetric behaviour at low frequencies is mainly determined by the behaviour of the continuous phase, it becomes possible to explain the behaviour of PS/PMMA blends from a limited number of hypotheses. The main hypothesis is that the PMMA layer next to the interface gelifies, while the PS layer next to the interface slips under the influence of a hydrodynamical field. The explanation concurs with all the experimental data which we obtained, regardless of the concentration of PS or PMMA. Moreover the effect of adding a block copolymer PS-b-PMMA can be explained.

Introduction

The results reported in this paper are part of a systematic research being done on the blending mechanisms of polystyrene (PS) and polymethylmethacrylate (PMMA) and on the influence of adding, during blending, a block copolymer (PS-b-PMMA). The resulting morphologies are quite different depending on the blending conditions. By a suitable choice of the parameters controlling the morphology, we observed the different forms mentioned in the literature, ranging from dispersions of spheroidal particles to those which are ellipsoidal, fibrillar or even lamellar (1)(2).

In this first paper we limit ourselves to blends containing spheroidal particles, in order to examine a simple case. This would not have been the case if we had included blends with highly anisodiametrical domains. We would then have to take into account the stability of such a morphology while the viscosity was being measured. Indeed, annealing, at the temperatures at which viscosities are measured and during times comparable to the time of such measurements, clearly influenced the morphology: elongated particles tend to more spherical forms and fibrillar or lamellar domains break due to a mechanism which was first investigated by Rayleigh (3) and treated theoretically later by Tomotika (4).

Experimental conditions and results

The PMMA was the commercial product Diakon MG 102 (ICI), having a molecular weight (M_n) of 44,000 g/mol and a polydispersity (I) of 2.32. The PS was the commercial product PNBOO (ORKEM) with M_n = 125,000 g/mol and I = 2.44. The block copolymer was made by ionic polymerisation by J.M. CATALA (Centre de Recherches sur les Macromolécules, Strasbourg). The characteristics of it were: M_n = 33,400 g/mol, I = 1.2 and a molecular weight of the PS block of 17,000.

The components were blended on a corotative twin-screw extruder namely the Clextral BC 21. The outside diameter of the screws was 25 mm. The temperatures of all the screw zones were 200 °C and that of the die 210 °C. More details of the experimental conditions can be found in S. Salier's report (5).

This paper examines the following samples:
sample 1: pure PS
sample 2: pure PMMA
sample 3_i: $(PS/BP)_i$, if i = 1, then the blend contained 7 % in weight of the block copolymer, abreviated BP; if i = 2, the concentration of BP was 17 %. These concentrations were chosen to have a global concentration of 5 % in weight of the block copolymer in the final (PS/PMMA) blend.
sample 4_i: $(PMMA/BP)_i$, blends of PMMA with BP, see 3_i for the signification of i.
sample 5: (PS/PMMA)(75/25), blend of PS and PMMA containing 75 % in weight of PS.
sample 6: (PS/PMMA)(25/75), blend of PS and PMMA containing 25 % in weight of PS.
sample 7: (PS/PMMA/BP)(75/25), blend containing 75 g of PS, 25 g of PMMA and 5 g of BP making a total of 105 g. The three components were introduced simultaneously in the extruder.
sample 8: ((PS+BP)/PMMA)(75/25), blend of the same composition as sample 7, but now the BP was first mixed with PS on the twin-screw extruder. The resulting blend, sample 3_2, was then added to the PMMA and past again through the twin-screw extruder.
sample 9: (PS/(PMMA+BP))(75/25), blend similar to blend 8, but the PS was first mixed with the PMMA.

The following samples:
sample 10: (PS/PMMA/BP)(25/75)
sample 11: ((PS+BP)/PMMA)(25/75)
sample 12: (PS/(PMMA+BP))(25/75)
are similar to samples 7, 8 and 9, but this time the main phase is the PMMA.

All samples were examined with a transmission electron microscope. Figure 1 reproduces the photographs of blends 7 and 10. Their were very similar to those of all the blends except blends 3_i and 4_i. The dark domains corresponded to the styrenic phases, the bright ones to the methacrylic phases. The photographs were treated with the help of image processing software, the result of which will be published later (6). It is presently sufficient to know that the dispersed particles were of spheroidal shape and that their dimensions ranged from about some tenths of a micron to a micron. The image processing analysis showed that the size of the particles, the distribution of the sizes and the distribution of the distances between particles varied from one sample to the other. Taking into account these variations were not essential for our interpretation, we assume them to be negligible.
The photographs of samples 3_i and 4_i indicated the presence of nodules of small photographic contrast which had a diameter on the order of one tenth of a micron. These were most probably block copolymer nodules insoluble in the homopolymer.
The viscosity measurements were made by Sylvie Salier (5) with a Rheometrics RM 605 rheogoniometer equiped with a plane-plane cell. The resulting dynamic

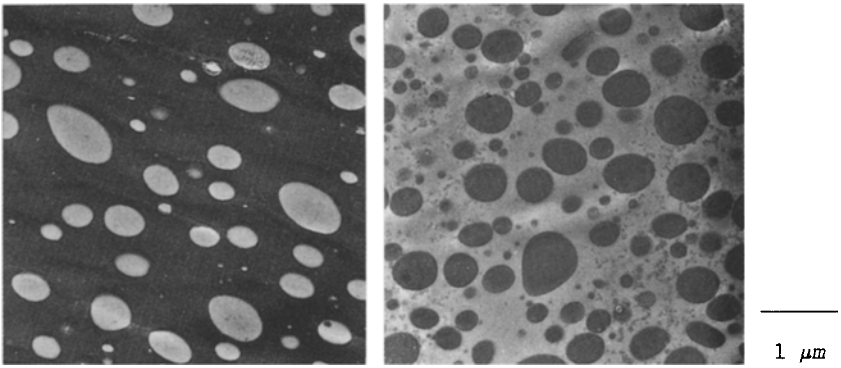

Figure 1 Blends 7 (PS/PMMA/BP)(75/25) and 10 (PS/PMMA/BP(25/75).

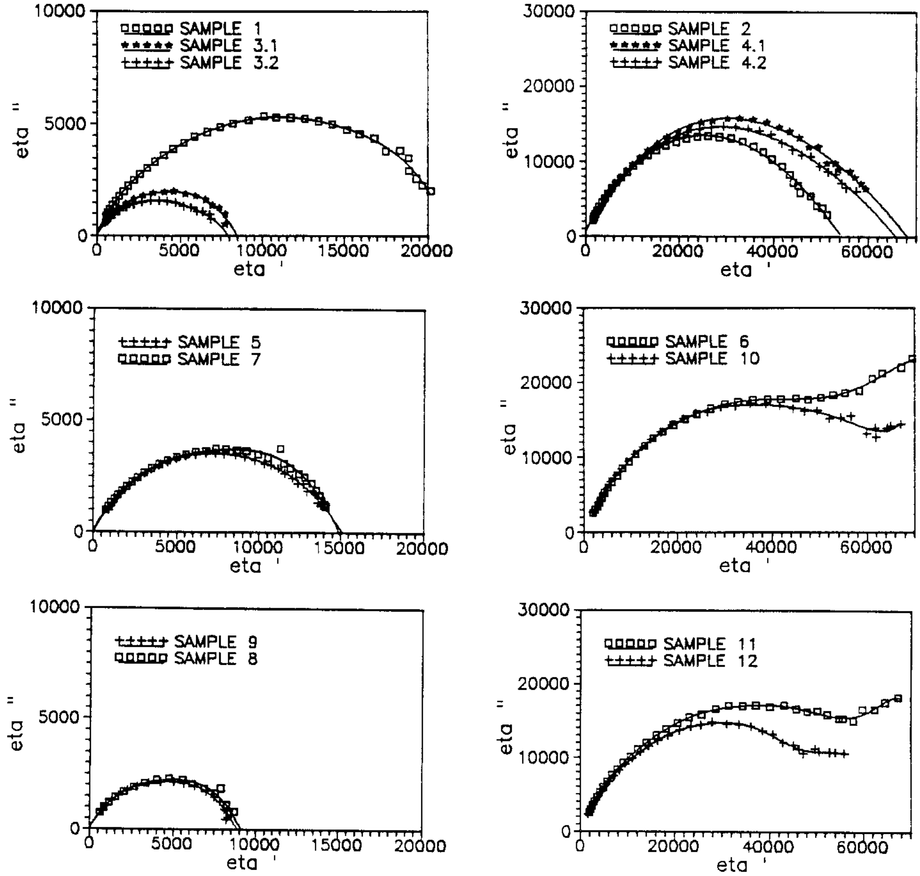

Figure 2 Cole-Cole diagrams of the 14 investigated samples.

viscosities were put into the form of Cole-Cole diagram (figure 2). On these diagrams the η'' component of the complex viscosity is given as a function of the η' component. The zero frequency viscosity, η_0, is the value of η' at the intersection of the Cole-Cole curve with the η' axis.
The principal results were the following:
- samples 3_i, $(PS/BP)_i$, have much lower η_0 values than those of PS: η_0 = 8,500 Pa.s for $(PS/BP)_1$ and η_0 = 8,000 Pa.s for $(PS/BP)_2$. For pure PS η_0 = 22,000 Pa.s. Note that the viscosity difference between the blends was small compared to the differences with the pure PS.
- samples 4_i, $(PMMA/BP)_i$, have η_0 values higher than that of PMMA: η_0 = 68,000 Pa.s for $(PMMA/BP)_1$ and η_0 = 66,000 Pa.s for $(PMMA/BP)_2$. For pure PMMA $_0$ = 54,000 Pa.s.
- sample 5, (PS/PMMA)(75/25), had η_0 lower than that of both components. Moreover the whole curve for sample 5 on the Cole-Cole diagram was under the curve corresponding to pure PS, which was the component having the lowest viscosity. The blend had η_0 = 14,800 Pa.s as compared with η_0 = 22,000 Pa.s for the pure PS.
-over the entire frequency range, sample 6, (PS/PMMA)(25/75), had a Cole-Cole diagram which was above that of pure PMMA. The PMMA was the component having the highest viscosity. At low frequencies the curve started to turn up which indicated the presence of a very low relaxation mechanism or of yielding. This phenomenon was already mentioned many times for blends, for example p. 137 in (7) as well as (8)(9) and (10). In general it was attributed to interfacial tension or to the appearance of a temporary, tridimensional network. A comprehensive analysis was given by Palierne (11), who improved Olroy's theory (12).
- sample 7,(PS/PMMA/BP)(75/25), had a Cole-Cole diagram which was practicaly the same as that of sample 5, (PS/PMMA)(75/25), with η_0 = 14,800 Pa.s.
- the curve of sample 8, ((PS+BP)/PMMA)(75/25), was under that of sample 7, near, but nevertheless a little above, those of samples 3_i. η_0 = 9,000 Pa.s.
- the diagram of sample 9, (PS/(PMMA+BP))(75/25), was nearly identical to that of sample 8.
- the behaviour of sample 10, (PS/PMMA/BP)(25/75), was similar to that of sample 6. Its Cole-Cole diagram, however, was slightly under that of 6.
- there were only small differences between the diagrams of samples 10 and 11, ((PS+BP)/PMMA)(25/75), but the diagram of sample 12, (PS/(PMMA+BP))(25/75), was lower than the preceeding ones and started to turn up at lower frequencies. Nevertheless, it remained higher than that of pure PMMA .

The Cole-Cole diagram of the pure block copolymer had not been determined: the moulded discs necessary for the viscosity measurements with the Rheometrics were too brittle.

Interpretation of the experimental results

At low frequencies the observations could be qualitatively explained if one assumed that:
- the macroscopic behaviour was mainly determined by that of the continuous phase. Vinogradov (13) had noted that "the flow properties of a two-phase blend

of incompatible polymers are first of all determined by the properties of the component which is the dispersion medium (continuous phase)". Other factors, such as the sizes of the particles, their distribution, the deformability of the particles, among others, played a secondary role.

- the block polymer remained, for the greatest part at least, in the phase in which it was introduced during the first mixing, although PS blocks as well as PMMA blocks were located at the interface.
- the behaviour at the interface was dominated by the viscometric properties of the layers near the interface. These properties were not identical on both sides of the interface. It has been supposed for a long time that, at the interface of two incompatible polymers, macromolecular chain elements of each component penetrate into the side of the other component. The penetration depth depends, among others, on temperature, time, molecular weights and thermodynamical interaction parameters of the components (degree of incompatibility). Theoretical analyses have been published not only on the repartition of two homopolymers A and B, but also on the repartition of copolymers, and especially of block copolymers added to A/B blends (14 to 17). Our hypothesis was that the PS chain elements, either from the homopolymer or from the copolymer, penetrated the PMMA phase. Doing so, they increased the viscosity of the penetrated layers in the limit to such a degree that these layers acquired a plastic behaviour comparable to that of a physical gel. We were not able to state precisely to what depth this penetration acts. If, as mentioned by some authors (2), PS and PMMA are partially compatible, the depth of this penetration may have been relatively important. It was also likely to depend on the mixing conditions. For our purpose it was assumed that this penetration was sufficient to modify the viscosimetric properties of the blend. The assumption seemed justified by the small distances between dispersed particles.

The hypothesis of the rigidification of the interface on the PMMA side agreed with the fact that most incompatible blends are positive deviation blends (PDB) (18), in other words the combined viscosity is higher than that predicted by a logarithmic addition rule. Nevertheless no satisfactory explanation for this positive deviation had been given so far in the general literature at the molecular level.

While the PMMA layers rigidified, we supposed that the layers on the PS side of the interface became more fluid due to the penetration of PMMA chain elements. As in the previous paragraphe, we were not able to estimate the depth of penetration. However, this depth was sufficient for modifying the viscosity properties of the blend. For the sake of simplification, we assumed in the following text that the decrease in viscosity in the layers on the PS side of the interface was such that it resulted in an interlayer slip. Utracki (p. 180 in (7)) explained that the behaviour of negative deviation blends (NDB), which represents the behaviour of about 30 % of immiscible blends, could be due to an increase of the specific volume of the blend at the interface. This dilatation may have resulted in an interlayer slip. Different authors have tried to give experimental proof of such a slip (for example (1)). Others have proposed a molecular model of the slippage mechanism (19)(20).

With the hypotheses just mentioned, especially the coexistence of layers of high viscosity (at the limit gelified) and of layers of low viscosity (at the limit slipping) at the interfaces, we have shown that it becomes possible, qualitatively at least, to explain all the experimental data we have reported and which are represented in figure 2.

So, for sample 3_i, $(PS/BP)_i$, the copolymer was dispersed as nodules in the PS matrix. The PMMA blocks at the surface of the nodules partially penetrated into the PS matrix which resulted in slippage at the interface, and, in turn, an important decrease of the viscosity. The reason why this decrease was of the same order of magnitude for both BP concentrations ought to be further investigated if one wants to obtain a quantitative explanation.

For the sample 4_i, $(PMMA/BP)_i$, the copolymer was dispersed as nodules in the PMMA. The PS blocks partially penetrate into the PMMA matrix. The PMMA layers at the interface rigidified leading to an increase of the vicosity. The fact that this increase was of the same order of magnitude for the two investigated concentrations was probably due to the same mechanism as the one which controlled the viscosity decrease for samples 3_i.

At the interfaces of the PMMA domains which were dispersed in the PS of sample 5, (PS/PMMA)(75/25), the layers on the PS side became less viscous. As PS was the continuous phase, a viscosity decrease of the blend resulted. This decrease ass less important than the one noted for samples 3_i. The influence of the concentration on the decrease could not be explained. Nevertheless, we suspected that the lower decrease for sample 5 could have been due to the higher molecular weight of the PMMA homopolymer than that of the PMMA blocks of the copolymer, and it could have been due to these blocks being linked to the PS blocks, which could have facilitated the penetration into the PS matrix.

On the other hand for sample 6, (PS/PMMA)(25/75), the layer on the matrix side rigidified leading to an increase of the blend viscosity. This effect was important enough to manifest itself as a gelation at zero frequency or, at least, as a very long time relaxation process. Contrary to what we mentioned for slippage and with the same caution concerning the unknown effect of concentration, the rigidifying effect was higher with the homopolymer than it was with the block copolymer.

In samples 7 and 10, (PS/PMMA/BP)(75/25) and (PS/PMMA/BP)(25/75), the block copolymer was introduced simultaneously in both phases. Under this condition we supposed that the dispersion of BP nodules was homogeneous throughout the blend. As a result the interfaces were practically unchanged in comparison to those of samples 5 and 6. That explained the behaviour of samples 7 and 10 are, respectively, almost identical to those of samples 5 and 6.

For sample 8, ((PS+BP)/PMMA)(75/25), the blend consisted of PMMA particles dispersed in a BP-rich PS matrix. In that matrix the BP is most probably dispersed as nodules. Under this condition, the PS at the PS/PMMA interface was not only fluidified by the PMMA homopolymer but also by the PMMA blocks of the BP which were at the interface. As mentioned above, these blocks were more efficient in the fluidifying process than the homopolymer. That explained why the viscosity of sample 8 was lower than that of sample 5.

The situation at the PS/PMMA interface of sample 9, (PS/(PMMA+BP))(75/25), is analogous to the one of sample 8, despite the copolymer being in sample 9 preferentially in the PMMA phase. As a result the behaviour of both samples was very similar.

Sample 11, ((PS+BP)/PMMA)(25/75), had a behaviour similar to that of samples 6 and 10. It was possible to explain this by the predominant rigidifying effect of the PS in the homopolymer in comparison to the effect of the PS blocks in the copolymer, which we had already mentioned. On the contrary, the Cole-Cole curve of sample 12, (PS/(PMMA+BP))(25/75), was under those of samples 6, 10 and 11, but above that of sample 2. We suspected that the high BP concentration on the PMMA side of the interlayer partially inhibited the rigidifying effect of the PS homopolymer.

Conclusions

In the literature there have been many observations which are in agreement with the hypotheses which have been presented. We will only mention one of these observations. Thornton et al. (21) prepared PS/PMMA blends on an elastic melt extruder. They observed that the T_g of PMMA increased while the T_g of PS decreased as a result of having added the PS to the PMMA. Naturally our investigations necessitate complementary systematic studies on the blending conditions as the observed effects are probably not the same for blends prepared from the melt as for blends from solutions, as well as studies on the effect of the nature and the molecular weight of the components. Nevertheless, the divere nature of the experimental results that have been explained by applying our hypotheses appeared to justify their publication at this stage of the investigation.

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