

Rheological investigation of form relaxation and interface relaxation processes in polymer blends

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SUMMARY

Transmission electron microscopical and rheological investigations have been performed on polymer blend systems of the type A/B, A/A-b-B/B, and A/C-b-B/B, where B is poly(methyl methacrylate) as the continuous and A is polystyrene as the dispersed phase. A-b-B is the corresponding diblock copolymer, and C-b-B is a diblock copolymer with poly(cyclohexyl methacrylate) (C) being thermodynamically miscible with A. The sphere-size distribution was estimated from the TEM data and found to be monomodal for all blends. Smaller sphere sizes in the A/C-b-B/B blends compared with the A/A-b-B/B blends prove the efficiency of the enthalpic acting compatibilizer.

The rheological material functions G' and G'' were used to calculate relaxation time spectra and to determine characteristic relaxation times. The form relaxation time τ_1 for the relaxation of the ellipsoidally deformed soft PS-particles back to spheres have been verified for all blends no matter whether they were compatibilized or not. An additional relaxation time τ_β was found for both types of compatibilized blends. This time is assigned to a non-isotropic interfacial stress, which may arise from relaxation processes of the block copolymers at the interface.

INTRODUCTION

Many important heterogeneous systems consist of droplets of a liquid dispersed in another one. Immiscible polymer blends of an appropriate component ratio can also be regarded as emulsions with the minor phase spherically dispersed. When such systems flow, the hydrodynamic forces can overcome the interfacial tension α_0 and cause the drops to change their shape (1). Interfacial tension tends to pull the drop back to a sphere, while the viscosity of the surrounding fluid slows down the motion. This process exhibits a characteristic form relaxation time τ_1 (2).

Immiscible polymer blends with high interfacial tensions suffer from an inherent problem, which derives from weak interactions, i.e., the poor adhesion between the phases. Adding block copolymer is one way to improve the interfacial situation (3, 4). Block copolymers can consist of blocks identical to those of the blend components, A-b-B, (here called entropic acting block copolymers) or they can contain blocks chemically different from the blend partners but miscible with them, A-b-D, C-b-B or C-b-D and we will call them enthalpic acting block copolymers. The latter type is supposed to show stronger interfacial activity (5-7). The addition of block copolymer to a polymer blend, among others, lowers the interfacial tension

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and therefore decreases the average particle size, prevent the droplets from coalescence, and influences the mechanical (including the impact) behavior.

In contrast to the influence of the amount of added block copolymer on the morphological properties, the influence on the viscoelastic properties, especially in the terminal relaxation region, is less investigated and, some times, contradictory (6, 8-12). The reasons for that may lie in the complex morphologies of the blends under investigation and in the difficulties with rheological measurements in the terminal relaxation region. In this relaxation region where the stresses are often at the limit of transducers sensitivity the changes in the interface due to the addition of compatibilizers can probably be seen. Nevertheless, it is also possible to study the segmental mixing of block copolymers in blends using other relaxation regions (13).

Thus, it is the aim of this investigation to analyze the influence of added block copolymers on the viscoelastic properties of the blends in its terminal relaxation region. Monodisperse polymers for the matrix, the inclusions and the compatibilizers are used for that purpose. Moreover, we will investigate whether it is possible to differentiate between enthalpic and entropic acting block copolymers.

This is a preliminary investigation in this field reporting about the principal properties of such systems. A more detailed analysis where the amount of added block copolymers is changed systematically is on the way.

EXPERIMENTAL

Materials

A narrowly distributed, anionically polymerized poly(methyl methacrylate), PMMA, was used as matrix material and a narrowly distributed polystyrene, PS, as the dispersed phase.

Table I: Molecular weight data for blend components and block copolymers. ^aDetermined from ¹H n.m.r.

Material	M _w , kg/mol	M _w /M _n	w _b , wt. %
PS	100	1.03	-
PMMA	31	1.19	-
P(S-b-MMA)	105	1.12	0.52 ^a
P(CHMA-b-MMA)	87	1.4	0.49 ^a

The two compatibilizers were anionically synthesized sym-

metric diblock copolymers i) P(S-b-MMA), A-b-B (13), and ii) P(CHMA-b-MMA), C-b-B, with cyclohexyl methacrylate, CHMA. Details concerning molecular weight, M_w, polydispersity, M_w/M_n,

and block composition (PMMA content), w_b, are listed in Table I.

For the investigations presented here, the systems A/A-b-B/B, and A/C-b-B/B with 92 wt % PMMA as matrix material, 7 wt % PS as dispersed phase and 1 wt % of the respective block copolymer were blended. A mixture without block copolymer with 92.5 wt % PMMA and 7.5 wt % PS was used as the neat (reference) blend. The blends were prepared by precipitation from solution of 10 wt % blend mixture in tetrahydrofuran into methanol. The precipitate was dried in vacuum for at least two days at 60°C. For rheological and morphological studies the blends were annealed for 30 min at 180°C in vacuum, and then molded to 1 mm thick disks with 25 mm diameter.

Transmission Electron Microscopy (TEM)

Ultrathin sections were made on a Leica Ultracut-E microtome. The sections were about 60 nm thick. Before imaging the sections were stained with RuO₄. From these samples, TEM elastic bright-field images were taken on a ZEISS CEM 902 (ESI mode). The morphology of the blends was analyzed using the image processing system IBAS 2.0 (Kontron).

Rheology

The rheological measurements were performed on a Rheometrics Mechanical Spectrometer RMS 800 using the parallel plate geometry. Isothermal frequency sweeps were recorded between 170°C and 230°C, in steps of 10°C. The isotherms were shifted to mastercurves and from these master curves relaxation time spectra were computed. The characteristic relaxation times are given by the position of the maxima in the terminal time domain. The relaxation times for the neat and compatibilized blends are listed in Table II.

RESULTS and DISCUSSION

Morphology by TEM

Two representative photographs of the blends are given in Figure 1 (a and b). The dispersed phase (PS) was visualized in all three blends investigated. When the spheres are cut by the microtome one gets the dimensions of the corresponding circular sections. The sphere-size distribution can be reconstructed from the section-size distribution according to a method developed by Gleinser et al. (14). Figure 2 shows the volume weighted sphere size distribution $v(R)$ of the neat blend. The integral calculated using this distribution function gives the volume percentage of dispersed material. Figure 2 shows that the distribution is monomodal with

Table II: Characteristic times, Newtonian viscosity and morphological data of neat and compatibilized blends.

Material	τ_1 , s	τ_β , s	η_0 , 10^{-5} Pas	R_v , nm	R_v/R_n
PS/PMMA	6.5	-	1.07	110	1.26
PS/PMMA with P(S-b-MMA)	3.9	41	1.10	90	1.16
PS/PMMA with P(CHMA-b-MMA)	5	50	1.14	65	1.18

a non-uniformity of $R_v/R_n = 1.26$. R_n is the number averaged particle radius and R_v the volume averaged. The distributions for the compatibilized blends are very similar and their characteristic radii are given together with that of the neat blend in Table II. This table shows that R_v decreased from 110 nm for the uncompatibilized blend to 90 nm for the blend containing 1 wt % P(S-b-MMA), and to 65 nm for the blend with the corresponding amount of P(CHMA-b-MMA). Although the dispersed particles are very small for the uncompatibilized blend the addition of the block copolymers leads to an even lower average particle radius. These data verify the dispersing efficiency of the block copolymers used. This effect is due to

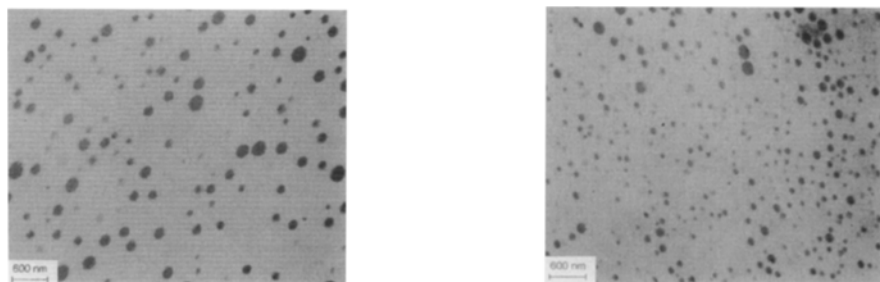


Figure 1: TEM images of the blends: a) 7.5% PS in PMMA and b) 7% PS and 1% P(S-b-MMA) in PMMA.

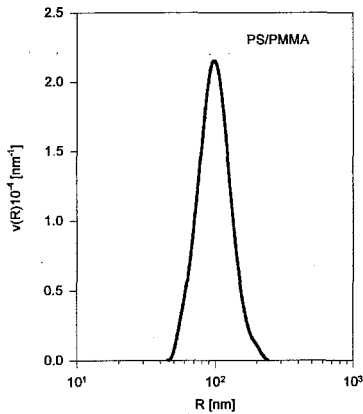


Figure 2: Volume weighted sphere-size distribution $v(R)$ of the blend with 7.5% PS in PMMA.

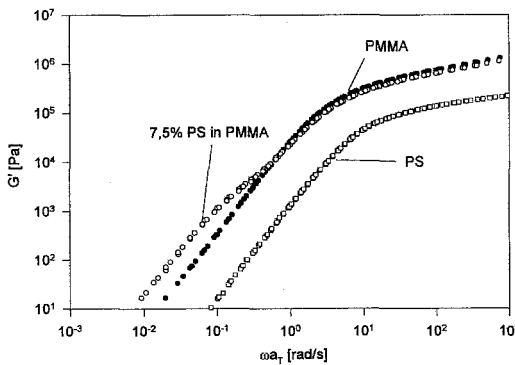


Figure 3: Storage modulus $G'(\omega)$ of the pure matrix material PMMA, the pure minor phase material PS and of the blend with 7.5% PS in PMMA. All data refer to a temperature of 190°C.

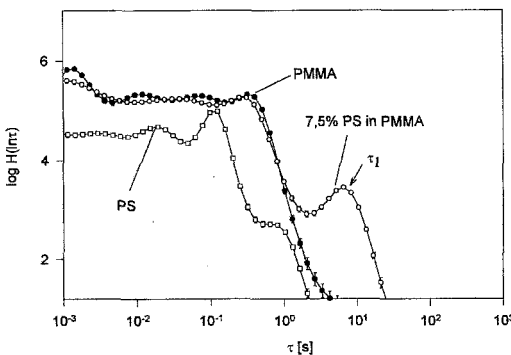


Figure 4: Relaxation time spectra of the materials given in Fig. 3.

the lowering of the interfacial tension by addition of block copolymer. It should also be pointed out that the blend with P(CHMA-*b*-MMA) has the smaller particles compared a blend with P(S-*b*-MMA) as interfacial agent. This is not a very large but significant difference. Nevertheless, it can be regarded as a hint on the better dispersing efficiency of the enthalpic acting block copolymer in comparison to the entropic acting block copolymer.

Rheology

Blend without Block Copolymer

In Figure 3 mastercurves of the logarithm of the storage modulus, G' , for the matrix PMMA, the dispersed phase PS and the blend consisting of 7.5 wt % PS in PMMA are plotted versus logarithm of the reduced frequency ωa_T . As can be seen, the blend shows an elastic contribution at lower frequencies in comparison to the blend components. The loss moduli are not presented because this material function is not susceptible to this relaxation process. In the corresponding relaxation time spectra (Figure 4) this process is more clearly seen and the spectrum presentation allows a quantitative determination of the characteristic form relaxation time τ_1 with a relative error of about 15 %. In a first approximation this time depends on the average volume weighted radius of the inclusions, R_V , the Newtonian viscosity of the matrix material η_m and the dispersed material η_d and on the interfacial tension α_0 (1). With ϕ the volume fraction of the dispersed phase and K the viscosity ratio η_d/η_m (approximately 0.1 in our case) the following equation holds (15):

$$\tau_1 = \frac{\eta_m R_V}{4\alpha^0} \frac{(19K+16)(2K+3-2\phi(K-1))}{10(K+1)-2\phi(5K+2)} \quad (1)$$

This relation can be used to calculate the form relaxation time. Similar relations have been used by other authors (2, 16). With an estimated interfacial tension of 2.0 mN/m (3, 17) a relaxation time of 6.5 s is calculated for the uncompatibilized blend. This value is in excellent agreement with the relaxation time estimated from the relaxation time spectrum (see Table II). Thus, it can be concluded that this relaxation process is really associated with the form relaxation of the inclusions.

Blends with Block Copolymer

In Figure 5 mastercurves of the logarithm of the storage module G' of the blends containing block copolymers are compared with that of the neat blend. The curves of the compatibilized

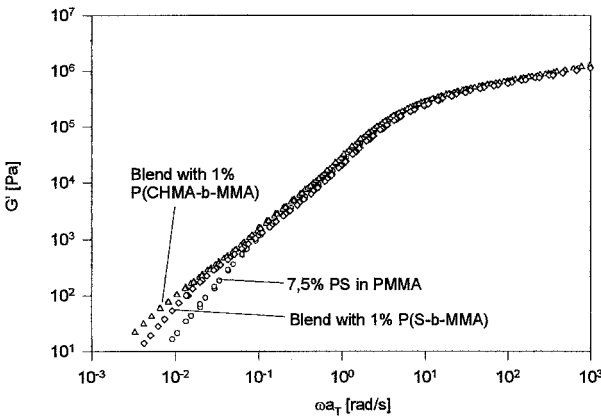


Figure 5: Storage modulus $G'(\omega)$ of the compatibilized blends compared to the uncompatibilized blend. All data refer to a temperature of 190°C.

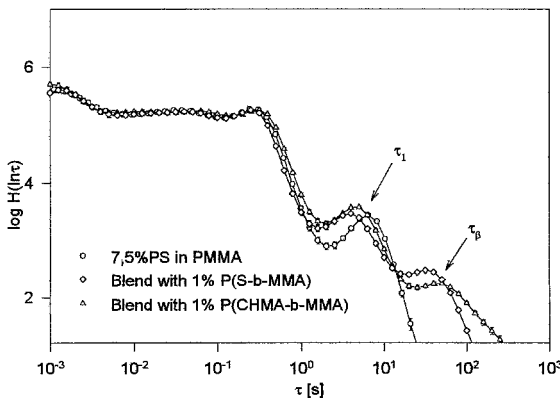


Figure 6: Relaxation time spectra of the materials shown in Fig. 5. An additional relaxation time τ_β appears.

blends deviate significantly from each other and give higher moduli at low frequencies compared to the moduli of the uncompatibilized blend. The moduli of the blend compatibilized with the enthalpic acting block copolymer are higher than the moduli of the entropic acting block copolymer. The same behavior is observed for the loss moduli not shown here. Significant differences in the Newtonian viscosity (rel-

ative error of about 2 %) between the neat blend and the blend compatibilized with P(CHMA-b-MMA) are the consequence. These data are given in Table II. Obviously, compatibilization leads to an higher viscosity compared to the uncompatibilized blend at least for the blend with the enthalpic acting block copolymer.

To find possible characteristic times inherent in the observed relaxation behavior, the relaxation time spectra are calculated for

the compatibilized blends also. These spectra and the comparison with that of the neat blend are presented in Figure 6. It is observed that the form relaxation times for the compatibilized blends deviate only slightly from that value observed for the neat blend. This invariance of the form relaxation time versus the added block copolymer is a consequence of its emulsifying and dispersing effectiveness. In accordance with Eq. 1 the interfacial tension reduces to the same amount as the averaged particle radius does. The analysis of the relaxation time spectra of the compatibilized blends shows also that the form relaxation time is no longer the terminal relaxation time. An additional characteristic relaxation time, described as τ_p , is the new feature in the spectrum of compatibilized blends. The characteristic times of that process are given in Table II.

It can be seen from that table that this additional relaxation time is ten times longer than the form relaxation time. Both relaxation processes are well separated. It can also be seen that the enthalpic acting block copolymer gives the higher characteristic time in comparison to the entropic acting block copolymer.

But what is the nature of τ_p ? The τ_p -value can not arise from an additional form relaxation time since the sphere-size distribution is monomodal. Apparently, this time constant is attributed to an additional interfacial stress, which may arise from migration and/or other relaxation processes of the block copolymers at the interface during macroscopical shearing. When the particles are ellipsoidally deformed, not only the surface area is increased. Certainly, the distribution of the block copolymers at the interface is no longer uniform. A relaxation time for re-establishment of distribution equilibrium is therefore conceivable and migration of interface-active molecules adsorbed at the interface should be possible (18). Another aspect is, that many entangled and/or enthalpically interacting molecules are involved in such a process which may require long times even though the rate of similar motions of an isolated molecule is short (19).

Up to now there does not exist any theory that directly links molecular processes as discussed above with rheological constitutive equations for the interface. But equations have been developed in the last years from a phenomenological point of view which allows to take into consideration relaxation processes, even at the interface.

Palierne (20) for example considered emulsions from such a point of view. In his model which represents a generalization of Oldroyds older findings (21), the interfacial stresses may be non-isotropic and depend on shear deformation induced variation of area in the following way:

$$\alpha_{ab} = \alpha_0 \delta_{ab} + \beta_{ab} \quad (2)$$

$$\beta_{ab} = \frac{1}{2} \beta' \gamma_{cc} + \beta'' (\gamma_{ab} - \frac{1}{2} \delta_{ab} \gamma_{cc}) \quad (3)$$

α_{ab} is the interfacial shear stress tensor, $\alpha_0 \delta_{ab}$ the equilibrium tension arising from the isotropic interfacial tension α_0 , β' a surface dilatation modulus, β'' a surface shear modulus and γ_{ij} the components of a surface strain tensor. In this model relaxation processes from block copolymers at the interface would manifest itself in the viscoelastic character of the surface stresses: $\beta_{ab} = \beta_{ab}(\lambda)$. The relaxation time λ was introduced by Palierne to account for such processes. This was the reason for us to designate the additional relaxation time found here as τ_p . Despite its phenomenological character, Palierne himself discussed such times in the context of disentanglement time of the block copolymers entangled with the matrix. Nevertheless, β' or β'' may offer basic approaches to describe phenomenologically further

characteristic relaxation processes. In future, this approach will be used to analyze the rheological data in more detail.

CONCLUSIONS

For diblock copolymer compatibilized blends of PMMA with PS as the disperse phase it was found that in addition to the form relaxation process of the spherical inclusions of PS, characterized by the time τ_1 , an additional relaxation process exists. Its characteristic time, τ_p , is ten times the form relaxation time in the case of the conditions used. It is supposed that the nature of τ_p is associated with migration and relaxation processes of block copolymers at the interface. From the phenomenological point of view, this relaxation time seems to correspond to the characteristic relaxation time λ which describes the viscoelastic character of surface stresses in Palierne's model.

In conclusion, further studies with variation of block copolymer concentration, block length, and the chemical constitution of the blocks should be performed. Only an enlarged data basis will help to understand of the rheological effect of macromoleculare surfactants in polymer blends.

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