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Influence of selective filling on rheological properties and phase inversion of two-phase polymer blends

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Abstract

We investigate the phase inversion of selectively filled polystyrene (PS)/poly(methyl methacrylate) (PMMA) blends prepared by melt mixing. As we have shown by transmission electron microscopy analysis and by the calculation of different selectivity criteria, the filler used (glass spheres of submicron dimensions) resides exclusively in the PMMA-phase and modifies its rheological properties correspondingly.

Four blend series made of PS and PMMA with different filler content are analyzed for the location of phase inversion concentration, ϕ_{PI}, and the width of the cocontinuity interval, CCI, in the concentration range where cocontinuity is predominant. Upon addition of filler a shift of ϕ_{PI} to higher concentrations of the filled PMMA-phase has been observed. This shift is in agreement with the predictions of a recently proposed equation defining the phase inversion concentration as that concentration where the maximum of the blends' extra elasticity occurs. The qualitative morphological analysis of these blends confirms this result.

Moreover, it was found that the cocontinuity interval is widened significantly at increased filler content. We explain the appearance of a wider CCI for filled blends on the basis of a slowdown of processes leading to morphology destruction. Corresponding Tomotika experiments (stability of fibrils) substantiate these findings. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Phase inversion; Selective filler; Viscosity ratio

1. Introduction

Polymer blends with cocontinuous morphologies have become a subject of great interest. The motivation for the specific morphology control in this field is the achievement of synergistic improvement of blend properties [1–4]. In order to produce cocontinuous blends it is of great importance to gain knowledge about the parameters influencing the concentration range within which cocontinuity is appearing. On the basis of the present knowledge the main influencing factors are blend composition ϕ, viscosity ratio p of the blend components, shear rates during mixing and mixing time.

A lot of work has been done to explore the effect of viscosity ratio on phase inversion concentration, ϕ_{PI} [5–10]. There are only few publications which analyze the influence of the elastic properties of blend components on phase inversion [11,12]. In a recent paper we have shown [13] that the role of viscosity ratio, p, and elasticity ratio, ψ, given in a broad frequency range, can be interchanged for the prediction of ϕ_{PI}. This is due to the same structural origin of both parameters and therefore these ratios cannot be varied independently.

Nevertheless our aim is to gain insight in the different influencing strength of elastic and viscous properties on phase inversion in order to better understand this process. Our idea was to modify the rheological properties of one blend component such that its elasticity and viscosity are changed in a different way in comparison to blends investigated so far. This can be realized by selective filling of one blend component with an appropriate filler which has smaller dimensions than the phase domains in the blend and thus hardly perturbs the domains during morphology development.

Filling of polymers with fillers of nanoscopic dimensions leads to a strong increase in elasticity of the compound, particularly above the percolation threshold of the used filler. The viscous properties are influenced less such that

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the correlation between viscosity and elasticity at least in a certain frequency range should be changed in comparison to the non-filled polymer.

There are only a few papers in the literature dealing with the effect of a selective filler on blend morphology, particularly on cocontinuous morphology. Gubbels et al. [14] investigated carbon black filled PE/polystyrene (PS) blends and detected an extension of the composition range in which cocontinuity is present compared to the non-filled system. During annealing at temperatures well above the melting temperature of PE the width of the cocontinuity interval is preserved in contrast to the system without filler. They explain the observed effects by a slowdown of coalescence kinetics during annealing with increased melt viscosity of the selectively filled PE-phase.

The group of Sumita et al. [15,16,32] have worked on conductive polymer blends. They correlated the degree of cocontinuity, determined by selective extraction techniques, with the conductivity of the blends filled with a conductive filler such as carbon black. The so called ‘second percolation threshold’, i.e. the blend composition at which such a blend becomes conductive due to formation of a cocontinuous morphology, is shifted to lower content of filled polymer and in the case of the filled systems this threshold was independent of post thermal treatment. They concluded that this finding can be explained by the enhanced viscosity of the filled component slowing down coalescence of this phase.

Cheah et al. [17] and Calberg et al. [18] investigated blend systems in which the filler is selectively located at the interface. Both groups observed that in this case the cocontinuous morphology is more stable during annealing or processing. Calberg et al. explained this finding with a slowdown of coalescence rate upon filling. Cheah et al. ascribed the enhanced stability to an unspecified interfacial effect of the filler.

Persson and Bertilsson [19] and Ljungqvist et al. [20] have found that in a certain concentration range filling of the minority component of a blend with a selective filler having a high aspect ratio, leads to continuity of this phase, provided that the viscosity of the minor phase is much lower than the viscosity of the majority polymer. They do not discuss possible scenarios of structure formation leading to the observed morphology.

All papers have one thing in common: the filler is not fully located in one phase but migrates to a certain extent into the second component and/or into the interface. Moreover, the filler concentration was held constant for each blend series. Thus the rheological properties of the filled component change with blend composition. An observed shift of ϕ_{PI} or broadening of the CCI may be caused to a certain extent by the increase of concentration of the filled component by addition of filler. These conditions are not suitable for a quantitative discussion of the influence of the rheological properties of the blend components on phase inversion.

To avoid these problems, our strategy is to use a fully selective filler, which is exclusively located in one blend phase. The filler content of this phase is kept constant within each blend series. In this way the rheological properties of the blend components are well defined and are the same for all blends of one series.

It is the aim of this paper to analyze the influence of a selective filler on the position and the width of the phase inversion interval of these blends. The results will be correlated with the rheological properties of the constituents.

We analyze the results in the light of a recently derived equation for the prediction of ϕ_{PI}. Changes in the $p-\psi$-correlation of filled blends in comparison to the non-filled blends will be used to elucidate mechanisms responsible for the observed effects.

2. Experimental

2.1. Materials

The polymers used were radically synthesized poly(methyl methacrylate) (PMMA) (PMMA 25 000, $M_{\mathrm{n}} = 15\,900$ g/mol, $M_{\mathrm{w}} = 30\,200$ g/mol, PD $= M_{\mathrm{w}}/M_{\mathrm{n}} = 1.90$, $\eta_0(200\ ^\circ\mathrm{C}) = 3300$ Pa s from Polysciences) and anionically synthesized polystyrene (PS) ($M_{\mathrm{n}} = 148\,800$ g/mol, $M_{\mathrm{w}} = 149\,300$ g/mol, PD $= 1.01$, $\eta_0(200\ ^\circ\mathrm{C}) = 3400$ Pa s kindly provided by BASF). The polymers were dried in a vacuum oven at 60 °C for at least 24 h before use. Glass spheres with very narrow particle size distribution (Monospheres 250A, particle diameter: 250 nm, density: 2.2 g/cm^3, no porosity, no surface treatment, Merck) were used as filler. The Monospheres were dried under high vacuum at room temperature for at least 24 h before use.

2.2. Preparation of composites

In order to obtain a homogeneous dispersion of the filler in the PMMA-phase, PMMA and Monospheres were first mixed in a Daca Micro-Compounder for 5 min at 200 °C and 100 rpm. Three types of filled PMMA with different filler content were prepared: PMMA with 10, 20 and 30 vol% Monospheres, which are denoted as PMMA-Mono*X*. *X* represents the volume percentage of Monospheres. The filled PMMA and the pure PMMA- and PS-granulates were milled to prepare a powder consisting of granules with a grain size of about 1 mm maximum. Note that the component consisting of PMMA and Monospheres in the blend is called ‘PMMA-phase’.

The blend components were then mixed at room temperature for 30 min in a tumble mixer. The sample preparation was carried out in a Randcastle single screw extruder RCP-MT250 equipped with a capillary die. The temperature of mixing was 200 °C. The average shear rate in the extruder was estimated on basis of geometrical parameters [34] to be around 12 s^{-1} and the maximum shear rate was in the range of 200 s^{-1}. For the capillary die with a radius of 1.25 mm and the given throughput of the extruder a shear rate value of about 5 s^{-1} was approximated. The residence time was constant for all blends and amounted to around 3 min.

For the morphological investigations the strands coming out of the die were immediately cooled to room temperature. The blend morphology is frozen instantaneously by this procedure because the glass transition temperatures of the blend components lie approximately 80 °C above quenching temperature.

For the preparation of samples for rheological measurement under the most sparing thermomechanical conditions the melt was directly extruded into a preheated cylindrical mold having the same temperature as the extruder. Additionally the blend material was annealed in the mold for a maximum of 1.5 min until the mold was filled completely. The mold containing the extruded disc was then subsequently quenched in water.

Four series of blends were prepared each consisting of at least six blends with varying composition in 10 vol% intervals around the phase inversion point estimated by the help of Utracki's equation [10]. The series are denoted as B12Mono*X*. *X* again represents the Monosphere content given in vol% and B12 is the blend introduced by Steinmann et al. [21].

One additional blend, which will be denoted as test sample, was prepared by one-step meltmixing as follows: Equal parts (by weight) of pure PMMA and PS and 5 vol% Monospheres referred to the total amount of polymers were melt-mixed in the Daca Micro-Compounder for 5 min at 200 °C and 100 rpm. The extruded and quenched strand was then prepared for transmission electron microscopy (TEM) investigation as explained later.

No signs of polymer degradation have been observed for the relevant time and temperature ranges (Fuchs et al. [35]).

2.3. Morphology

The blends were prepared for TEM by cutting ultrathin sections of the extruded strands perpendicular to the flow direction of minimum 60 nm thickness (as estimated from interference colors) using a Leica Ultracut-E microtome with a diamond knife. As we have shown in a recent publication [13] the investigation of the morphology in the cutting plane perpendicular to flow is sufficient to get results which are representative for the three-dimensional morphology. The microtoming was followed by selective staining of the PS phase with gaseous ruthenium tetraoxide (RuO_4) [22]. TEM elastic bright field images were taken on a Zeiss CEM 902, operating at 80 kV. In the images the stained PS domains appear dark gray, the domains consisting of PMMA light gray and the Monospheres are black. Silicon specific energy dispersive X-ray (EDX)-imaging was performed with a Zeiss CEM 912 at 120 kV, equipped with an EDX detector.

2.4. Rheological testing

The rheological measurements were carried out on a CVO rheometer (Bohlin) using parallel plate geometry (plate diameter of 25 mm). The blend components were rheologically characterized by recording frequency sweeps at different temperatures at a strain amplitude of approximately 1%. The software 'Lsshift' was used to create mastercurves at 190 °C (corresponding to the rheological testing temperature of the blends) and 200 °C (corresponding to processing temperature for blend preparation). The dynamic viscosity and the storage modulus of the blend components at 200 °C are shown in Fig. 1(a) and (b).

The blends themselves were measured only at one temperature. This temperature was chosen on the one hand to guarantee stability of the morphology during time of measurement, and on the other hand to access the terminal region at measurement times as short as possible. For these reasons we have chosen a measurement temperature of 190 °C which is lower than processing temperature. TEM images before and after rheological testing revealed that morphology did not change significantly within the time

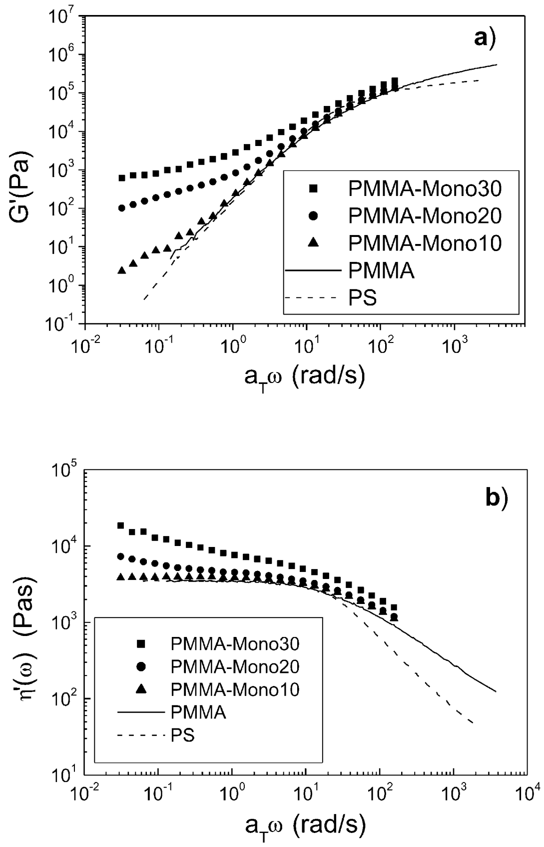

Fig. 1. (a) and (b) Storage modulus and dynamic viscosity of neat PS and PMMA and of the filled PMMA-composites as functions of frequency at a reference temperature of 200 °C corresponding to processing temperature.

scale of this isotherm. We performed all measurements at low strain amplitudes (about 0.5–1%) in order to minimize mechanical destruction or change of morphology. The heating chamber was purged with nitrogen to avoid decomposition of the polymers.

3. Results and discussion

3.1. Selectivity of filler

At first, we want to prove the selectivity of the nanoparticles used for the example of the test sample, i.e. the one-step blend.

In Fig. 2(a) TEM image of the test sample, and in Fig. 2(b) the TEM image with the corresponding overlay of the silicon-specific EDX-image of this blend are shown. The light gray domains in Fig. 2(a) consist of PMMA, the surrounding dark gray phase represents the stained PS, which forms the matrix and the black objects within the light gray domains are the Monospheres. To differentiate clearly between Monospheres and PS, silicon specific images were recorded by EDX technique coupled with TEM. The result of this technique is shown in Fig. 2(b) where the silicon-rich areas appear as clusters of white spots inside the black objects representing the Monospheres in the TEM image lying beneath. The single white spots spreading over the whole image are caused by noise. Fig. 2(b) reveals that the Monospheres (clusters of white dots) are exclusively located in the PMMA-phase (light gray). Note that the difference in phase dimensions between the blend in Fig. 2 and the blends in Fig. 3 is due to different processing conditions. To guarantee a good dispersion of filler particles within the polymer the one-step blend as well as the PMMA-phase (PMMA + Monospheres) were produced in a conical twin screw extruder (Daca Micro-Compounder) which exerts a more intense shear than the extruder used for the preparation of the blends under investigation.

The experimentally found selectivity of our filler can be explained by the application of different criteria evaluating the interaction between filler and polymers in ternary blends.

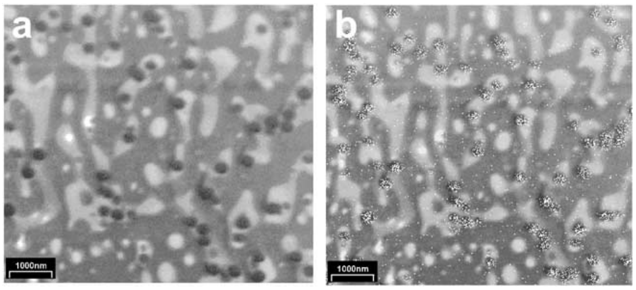

Fig. 2. (a) TEM image of a Monosphere-filled blend, with PMMA as light gray, PS as dark gray phase (stained with RuO_4) and Monospheres as black circles. (b) Overlay of Si-specific EDX-image (white dots) and the corresponding TEM image.

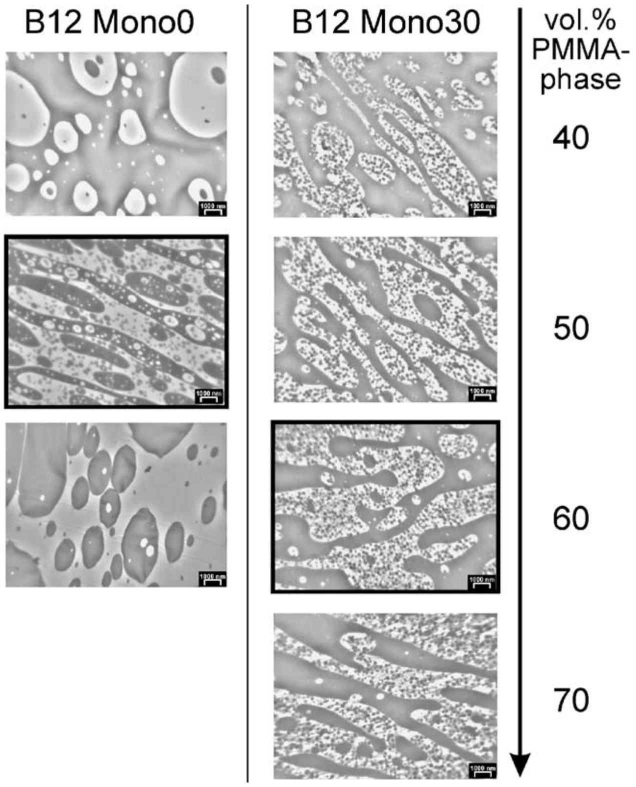

Fig. 3. Comparison of blends of series B12Mono0 (non-filled) and B12Mono30 with PMMA-phase concentrations of 40–70 vol%. The light domains contain PMMA, PS appears dark gray (stained with RuO_4) and Monospheres are visible in the filled blends as small dark gray circles (not to be differentiated by color from stained PS) within the light domains. The blends at the respective phase inversion point are emphasized by a frame.

Schuster et al. [23] have shown that the driving force in competitive adsorption of two different polymers on the filler surface (in their work: carbon black) can be related to the difference of the corresponding solubility parameters, δ. The smaller this difference the greater is the affinity of the polymer to the filler. Premphet and Horanont [24] have confirmed this thermodynamic approach. They showed that in filled blends with two immiscible polymers their filler (calcium carbonate) distributes selectively in the polymer-phase with which it has the lowest interfacial tension.

An extension of this qualitative approach is provided by Sumita et al. [15]. They introduce a wetting coefficient, called ωa, which allows to predict selectivity of the filler:

$$\omega a = \frac{\gamma_{\text{filler}-\text{B}} - \gamma_{\text{filler}-\text{A}}}{\gamma_{\text{A}-\text{B}}}. \tag{1}$$

In Eq. (1) $\gamma_{\text{filler}-\text{A}}$ and $\gamma_{\text{filler}-\text{B}}$ are the interfacial tensions between the filler and polymer A or B and $\gamma_{\text{A}-\text{B}}$ is the interfacial tension between polymers A and B. If $\omega a > 1$ the filler distributes within the A-phase, if $-1 < \omega a < 1$ the filler is located at the interface and if $\omega a < -1$ the filler is selective for the B-phase. Hobbs et al. [25] introduced a similar concept for ternary blends, which is based on the spreading coefficient, $\lambda_{\text{A}-\text{C}}$, representing a measure for the tendency of polymer A to encapsulate dispersed domains of

Table 1
Surface tensions at 200 °C of the polymers [26] and the filler [27] used

Material	Surface tension (mN/m)		
	Total (γ)	Disperse component (γ^d)	Polar component (γ^p)
PS	27.8	23.1	4.7
PMMA	27.4	19.7	7.7
SiO_2	257.7	94.7	163.0

a second polymer C in a matrix of a third polymer B:

$$\lambda_{A-C} = \gamma_{B-C} - \gamma_{A-B} - \gamma_{A-C}. \tag{2}$$

The γ_{i-j} are the interfacial tensions between the different polymer pairs. Encapsulation takes place if the spreading coefficient is positive and the encapsulation tendency of polymer A increases with increasing values of λ_{A-C}. This concept is transferable to blend systems consisting of two immiscible polymers A and B and a filler. In this case in Eq. (2) polymer C is replaced by the filler, which is encapsulated by one of the polymers.

Now, we calculate the necessary interfacial tensions, γ_{A-B}, to assess the usability of criteria. The interfacial tensions between PS and PMMA are determined with the harmonic mean equation of Wu [26,33] (Eq. (3)) where A and B are the two polymers:

$$\gamma_{A-B} = \gamma_A + \gamma_B - \frac{4\gamma_A^d\gamma_B^d}{\gamma_A^d + \gamma_B^d} - \frac{4\gamma_A^p\gamma_B^p}{\gamma_A^p + \gamma_B^p}. \tag{3}$$

Here γ_A and γ_B are surface tensions of the two materials in contact, and d and p superscripts denote the dispersion and polar components of the surface tensions.

For the calculation of the interfacial tensions between filler and polymers the geometric mean equation of Wu [26] (Eq. (4)) is used since it is recommended for systems of a high-energy material, SiO_2-spheres, and a low-energy material, such as the polymers used:

$$\gamma_{A-B} = \gamma_A + \gamma_B - 2\left(\gamma_A^d\gamma_B^d\right)^{1/2} - 2\left(\gamma_A^p\gamma_B^p\right)^{1/2}. \tag{4}$$

The corresponding values of the surface tensions at 200 °C are taken from literature [26,27] and are listed in Table 1. The resulting interfacial tensions for the possible pairs are given in Table 2.

Table 2 reveals that the interfacial tension between Monospheres and PS is by 8.8 mN/m larger than the respective value for the pair Monospheres–PMMA. According to Refs. [23,24] this indicates a larger affinity of the filler to the PMMA-phase than to PS in the blend. The concept of the wetting coefficient confirms this tendency, too: Eq. (1) yields a wetting coefficient of 8.7.

Calculations of the spreading coefficient on basis of Eq. (2) yield the following results: With A = PS, B = PMMA and C = Monospheres the spreading coefficient λ_{A-C} amounts to 7.9 mN/m and for A = PS, B = PMMA and C = Monospheres to −9.9 mN/m. According to these calculations PMMA tends to encapsulate the Monosphere particles in the case of PS forming the matrix, whereas PS does not encapsulate the filler if the matrix is PMMA.

Table 2
Interfacial tensions between the possible polymer–polymer- and polymer–filler-pairs. The interfacial tensions between the polymers are calculated with the harmonic mean equation (Eq. (3)) and those between the filler and a polymer with the geometric mean equation (Eq. (4)). The surface tensions are taken from Table 1

Possible pairs	Interfacial tension γ_{A-B} (mN/m)
PMMA/PS[a]	1.02
PMMA/SiO_2[b]	127.9
PS/SiO_2[b]	136.8

[a] Calculated with harmonic mean Eq. (3).
[b] Calculated with geometric mean Eq. (4).

This quantitative analysis confirms and explains our experimental findings. It clearly shows that our chosen filler is fully selective for PMMA. On this basis we are able to exclude significant migration of the filler during processing and rheological measurement and to keep the rheological properties of the filled phase constant and consequently well defined.

3.2. Morphological properties: qualitative analysis

In Fig. 3, the morphology of some non-filled blends is compared with that of the filled blends of the series B12Mono30 at the given concentration of the PMMA-phase.

The non-filled blend series B12Mono0 clearly displays phase inversion at PMMA-concentrations around 50 vol%. At this concentration the PS- and the PMMA-phase are continuous whereas the two other blends show a dispersion morphology. In the case of the filled blend series (B12Mono30) with 50, 60 and 70 vol% PMMA-phase, it cannot be specified which component forms the matrix, they are all cocontinuous. A dispersion morphology is found for the blends of this series with a PMMA-phase content of 40 and 80 vol% (not shown). In these two blends the dispersed domains are more elongated and more irregular than those in the case of the corresponding non-filled blends.

The phase inversion concentration $\phi_{PI,PMMA}^{morph}$ of the blend series are estimated qualitatively by detecting the co-continuous blends of one series by means of the criterion that none of the components forms the matrix, and then determining the center of this cocontinuity interval. The resulting $\phi_{PI,PMMA}^{morph}$-values are listed in Table 3. A recently presented method of the quantitative morphological ϕ_{PI}-determination based on form factor analysis [13] was not applicable here because of the difficult sample preparation for TEM and the difficult image analysis due to the nanoparticles.

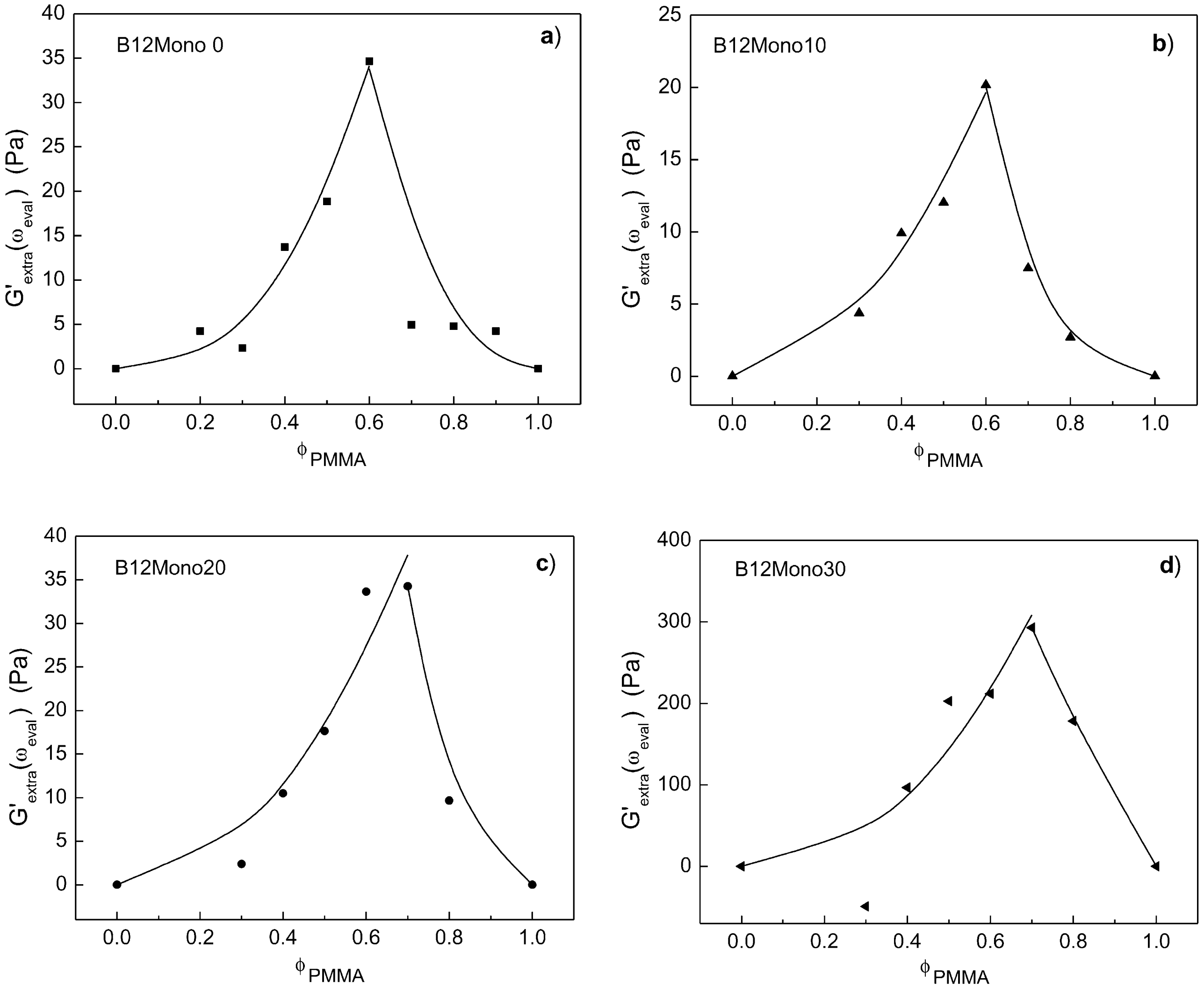

Fig. 4. (a)–(b) Evaluation of the elastic criterion maximum of G' at the frequency $\omega_{\text{eval}} = 0.0044$ rad/s at 190 °C dependent on volume ratio of PMMA-phase of the blends. The fit curves according to Eq. (7) are represented by lines. The resulting fit parameters a and z are given in Table 3.

Nevertheless, from this comparison of TEM-images two main changes in morphology can be detected: Firstly, we observe a broadening of the CCI upon addition of selective filler. This broadening sets in at filler concentrations of 20 vol% (not shown) refered to the PMMA-phase and manifests at 30 vol% filler.

Table 3

Comparison of phase inversion concentrations determined by morphological analysis with the results obtained by evaluation of the two rheological criteria, maximum of G' and maximum of η'

Blend series	Morphology[a]	Rheology[a]	
	$\phi^{\text{morph}}_{\text{PI,PMMA}}$	$\phi^{\max\ \eta'}_{\text{PI,PMMA}}$	$\phi^{\max\ G'}_{\text{PI,PMMA}}$
B12Mono0	50	60	60
B12Mono10	50	70	60
B12Mono20	60	70	70
B12Mono30	60	70	70

[a] All values in vol% PMMA-phase (=PMMA + Monospheres).

Secondly, the phase inversion point, defined as maximum of cocontinuity at the center of the CCI, is shifted from 50 to 60 vol% PMMA-phase. This shift becomes prominent for the series containing 20 vol% of filler or more.

These results are based on qualitative morphological evaluation. In order to quantify the influence of selective filling on phase inversion we analyze the rheological properties of the blends.

3.3. Rheological properties: quantitative determination of ϕ_{PI}

As we have shown in a previous paper [21], there are rheological criteria based on viscous and elastic properties of the blends, 'maximum of η'' and 'maximum of G'', respectively, which are suitable for the detection of the phase inversion concentration in non-filled blend series. We have shown for non-filled blends that the maximum of the corresponding storage modulus at a given evaluation frequency (for its definition see Ref. [21]), ω_{eval}, indicates the maximum of cocontinuity, the phase inversion concentration. Here we want to refine these criteria and apply them to the filled blends. Again, as in our recent paper, we use an evaluation frequency rather than an evaluation stress (G''_{eval}). Knowing that some authors (Utracki [10,28]) prefer the second method, because stresses and not rates are continuous across interfaces, we found that the first method is better suited to discriminate between the characteristic viscosities as well as between the characteristic moduli for different concentrations. In the following we will first test the criterion maximum of G', which is based on the maximum of the blend's elastic extra stresses at phase inversion concentration.

Due to the fact that filling increases the viscosity and elasticity of blend components to a level which is of same order of magnitude as the extra contributions originating from the interface, we are forced to separate the contributions (Eq. (5)). The corresponding moduli, G'_{extra}, were derived assuming the following relationship between the measured storage moduli of the blends, G'_{blend}, and the assumed storage moduli of the mixture, G'_{mix}

$$G'_{\mathrm{extra}}(\omega_{\mathrm{eval}}) = G'_{\mathrm{blend}}(\omega_{\mathrm{eval}}) - G'_{\mathrm{mix}}(\omega_{\mathrm{eval}}), \tag{5}$$

with

$$G'_{\mathrm{mix}}(\omega_{\mathrm{eval}}) = \phi_{\mathrm{PMMA}} G'_{\mathrm{PMMA}}(\omega_{\mathrm{eval}}) + (1 - \phi_{\mathrm{PMMA}}) G'_{\mathrm{PSoderPSAN}}(\omega_{\mathrm{eval}}). \tag{6}$$

In contrast to a recent publication [21], here we use a linear mixing rule for the estimation of G'_{mix} because it accounts more realistically for the influence of the components on rheological properties of the blends over the entire composition range than expressions which are only valid in a rather small range.

In Fig. 4(a)–(d) the extra storage moduli of the blends at the evaluation frequency are plotted versus blend composition, i.e. volume fraction of PMMA-phase. This figure shows that the extra storage moduli of the blends, G'_{extra}, increase from both sides and meet in a maximum. Similar to the non-filled blends, the phase inversion concentration is determined by the volume fraction of PMMA-phase at this maximum. The corresponding values of $\phi_{\mathrm{PI,PMMA}}^{\max G'}$ are given in Table 3.

According to this criterion the phase inversion concentration is shifted due to filling towards higher concentrations of PMMA-phase (from 60 for the non-filled to 70 vol% PMMA-phase) at a filler concentration of about 10–20 vol% related to the PMMA-content.

We apply the following formula for the calculation of extra storage moduli in dependence on the matrix viscosity η_{m}, interfacial tension α and evaluation frequency ω_{eval}:

$$G'_{\mathrm{extra}}(\omega_{\mathrm{eval}}) = \frac{\eta_{\mathrm{m}}^2 \omega_{\mathrm{eval}}^2}{3\alpha} a\phi^z. \tag{7}$$

For details concerning the derivation of Eq. (7) see Steinmann et al. [21]. This equation contains two free parameters, a and z, which are related to the specific interfacial area, Q and to the parameter λ, controlling the degree of total relaxation (Lee and Park [29]).

Table 4
Free parameters a and z from fitting Eq. (7) to the experimental data of G'_{extra} to the left and right of G'_{extra}-maximum

Blend series	a (m)		z	
	Left	Right	Left	Right
B12Mono0	5.2×10^{-4}	7.5×10^{-4}	2.76	2.50
B12Mono10	2.1×10^{-4}	6.0×10^{-4}	2.06	3.25
B12Mono20	3.1×10^{-4}	4.7×10^{-4}	2.17	3.12
B12Mono30	2.6×10^{-3}	1.3×10^{-4}	2.32	1.22

In order to examine whether or not the criterion maximum of G' is suitable for the filled blends, Eq. (7) (with $\omega_{\mathrm{eval}} = 0.0044$ rad/s and $\alpha = 1.1$ mN/m [33] is fitted separately to the experimental data to the left and to the right of G'_{extra}-maximum each including the maximum G'_{extra}. The respective fits are marked with lines in Fig. 4(a)–(d) and the resulting fit parameters a and z for the left and right side are given in Table 4.

The z- and a-values will be discussed later. Fig. 4 makes clear that the G' criterion developed on basis of non-filled blends is excellently applicable to the selectively filled blends, too, and works well with blend series having very small or large elasticity ratios. For very different elasticity between both blend components the experimental determination of the phase inversion concentration might become difficult because the extra contribution will be small in comparison to the corresponding matrix component. For the blends investigated so far we did not face with this problem.

As it is known from literature [21,28] the blend viscosities are also suitable for the quantitative determination of ϕ_{PI}. The criterion maximum of η' (at the phase inversion concentration) which was valid for non-filled blends with $|\log p| < 1$ should be also applicable to the present blend series.

Fig. 5 shows the composition dependence of the dynamic blend viscosity at the evaluation frequency ($\omega_{\mathrm{eval}} = 0.0044$ rad/s). The viscosities of the blends lie well above the respective linear logarithmic additivity rule, marked as dashed straight line. The full lines link the data points of each blend series and are drawn to guide the eye.

Blend viscosity increases from both sides with increasing concentration of second blend component and reaches a maximum, which represents the phase inversion point as we have shown recently [21]. The phase inversion concentration $\phi_{\mathrm{PI,PMMA}}^{\max \eta'}$ is determined from this maximum and the values are given in Table 3. The evaluation of the viscous blend properties reveals a shift of ϕ_{PI} from 60 to 70 vol% PMMA-phase upon addition of filler.

In Table 3 the values of ϕ_{PI} obtained by qualitative morphological and quantitative rheological evaluation are compared. As Table 3 shows there is a good agreement

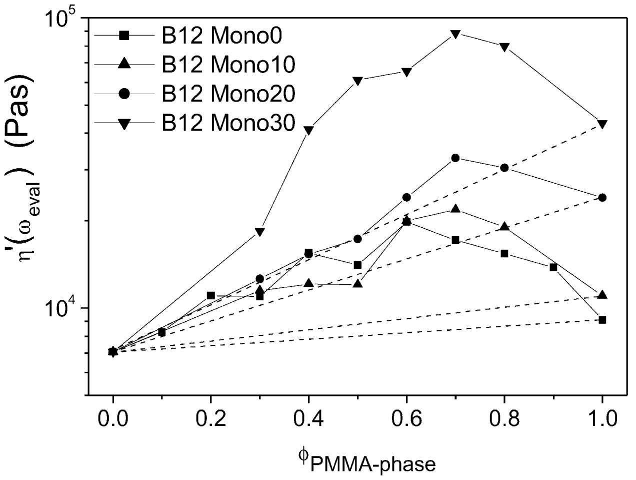

Fig. 5. Viscous criterion maximum of η' evaluated at the frequency $\omega_{\rm eval} = 0.0044$ rad/s at 190 °C dependent on blend composition (volume ratio of PMMA-phase).

between the morphological and rheological results concerning the shift of the phase inversion concentration by 10 vol% PMMA-phase caused by the addition of filler. They differ slightly in the position of $\phi_{\rm PI}$. The morphological analysis and the evaluation of the criterion maximum of G', agree in the concentration of filler at which the shift of $\phi_{\rm PI}$ becomes significant (20 vol%); the criterion maximum of η' yields a smaller value (10 vol%).

From this comparison we conclude that the rheological criteria developed on the basis of non-filled blend systems are applicable to filled systems as well. However, as we have discussed recently [21] we will use the rheologically determined phase inversion concentrations because rheology detects the three-dimensional bulk properties better than morphological analysis based on two-dimensional sections. This might explain the slight discrepancy between morphological and rheological analysis concerning the position of $\phi_{\rm PI}$.

Since for a large number of blend series the criterion maximum of G' has proved to be the most suitable rheological criterion [21], we will use the phase inversion concentration value determined by application of this criterion, $\phi_{\rm PI,PMMA}^{\max G'}$, in the following.

3.4. Influence of viscosity- and elasticity-ratio on the phase inversion concentration

We have found that by selective filling of PMMA the phase inversion concentration, $\phi_{\rm PI,PMMA}^{\max G'}$, is shifted to higher concentrations of PMMA-phase. According to theory [28], in blend systems with viscosity ratios (and according to Fig. 6 with elasticity ratios) differing significantly from 1.0 the phase inversion concentration is shifted towards higher concentrations of the more viscous (elastic) phase. The less viscous (elastic) phase tends to encapsulate the phase with higher viscosity.

The effective viscosity ratio $p_{\rm eff}$ and the effective

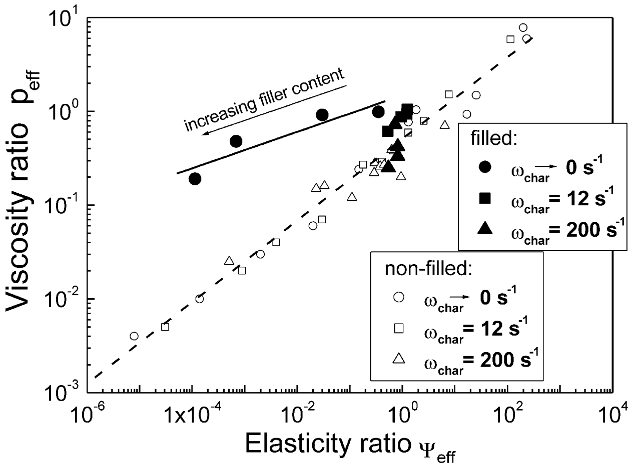

Fig. 6. Correlation between the effective elasticity ratios and the effective viscosity ratios of the blend series at different characteristic frequencies at 200 °C (processing temperature). The two straight lines are linear fits of the respective experimental data.

elasticity ratio $\psi_{\rm eff}$ at a certain characteristic frequency are defined as follows:

$$p_{\rm eff} = \left.\frac{\eta'_{\rm PS}(\omega)}{\eta'_{\rm PMMA}(\omega)}\right|_{\omega=\omega_{\rm char}} \tag{8}$$

and

$$\psi_{\rm eff} = \left.\frac{G'_{\rm PS}(\omega)}{G'_{\rm PMMA}(\omega)}\right|_{\omega=\omega_{\rm char}}. \tag{9}$$

There are three characteristic frequencies we are interested in: the frequency which corresponds to nearly zero shear conditions, $\omega_{\rm char} \rightarrow 0\ {\rm s}^{-1}$ and the two frequencies corresponding to the average shear rate ($\omega_{\rm char} = 12\ {\rm s}^{-1}$) and to the maximum shear rate during processing ($\omega_{\rm char} = 200\ {\rm s}^{-1}$), as described in Section 2.

The $p_{\rm eff}$- and $\psi_{\rm eff}$-data of eleven non-filled blend series (Steinmann et al. [13], open symbols) and the blend series B12Mono0, B12Mono10, B12Mono20 and B12Mono30 (full symbols) are given in Fig. 6. In addition, these values are given in Table 5.

The dashed straight line in Fig. 6 marks the p–ψ-correlation for the non-filled blend systems. It is independent of the chosen characteristic frequency and described by $p \propto \psi^{\alpha}$ with $\alpha \approx 0.5$. The full straight line represents the p–ψ-correlation for the filled blend series at zero shear rate conditions.

It can be recognized that the data for filled blends, independent of filler content, at characteristic frequencies between 12 and 200 rad/s follow the same correlation as the non-filled series. Consequently, selective filling has no significant effect on the p–ψ-correlation under shear rates predominant in the extruder.

Under zero shear conditions the situation is changed: the data of the filled blend series deviate significantly from the p–ψ-correlation of the non-filled series.

In Fig. 7 the experimentally found phase inversion

Table 5
Viscosity and elasticity ratios of the blend components at 200 °C (processing temperature) at three different characteristic frequencies which correspond to the approximated shear rates in the extruder or to nearly zero shear conditions

Blend series	$p_{\mathrm{eff},0}$ [a]	$p_{\mathrm{eff},12}$ [b]	$p_{\mathrm{eff},200}$ [c]	$\psi_{\mathrm{eff},0}$ [a]	$\psi_{\mathrm{eff},12}$ [b]	$\psi_{\mathrm{eff},200}$ [c]
B12Mono0	1.03	1.03	0.42	0.35	1.25	0.82
B12Mono10	0.91	0.94	0.33	0.03	1.22	0.82
B12Mono20	0.48	0.87	0.32	6.9×10^{-4}	0.95	0.73
B12Mono30	0.19	0.61	0.25	1.1×10^{-4}	0.54	0.54

[a] Values taken at $\omega_{\mathrm{char}} = 0.0044\ \mathrm{s}^{-1}$.
[b] Values taken at $\omega_{\mathrm{char}} = 12\ \mathrm{s}^{-1}$.
[c] Values taken at $\omega_{\mathrm{char}} = 200\ \mathrm{s}^{-1}$.

concentrations, $\phi_{\mathrm{PI,PMMA}}^{\max G'}$, are shown in dependence on viscosity ratio together with some calculated and previously given values. The scattering of the experimental data of the various blend series is distinct but within the known limits (Utracki [10]). The results for the 12 non-filled blend series, including B12Mono0, are drawn for the viscosity ratios at the two extremal shear rates (zero shear and maximum shear rate in the melt blending equipment). The phase inversion concentrations of series B12Mono0 and B12Mono30 were taken from the evaluation of the rheological criterion maximum of G' (Table 3). Addition of selective filler increases the viscosity of the PMMA-phase and thus decreases the viscosity ratio. Consequently, ϕ_{PI} has to be shifted to higher concentrations of PMMA-phase. The observed shift of $\phi_{\mathrm{PI,PMMA}}^{\max G'}$, by 10 vol% PMMA-phase at a filler content of 20 vol% referred to PMMA is in agreement with our developed criterion for non-filled blends [13].

The calculated lines presented in Fig. 7 are based on our recently derived equation [21]:

$$\phi_{\mathrm{PI,PMMA}} = \frac{1}{p^{1/z} + 1}. \qquad (10)$$

An average z-value of 4.8 (full line in Fig. 7) was obtained from the morphological evaluation (Steinmann et al. [21]) of 11 non-filled blend series. The other z-values used in this chart were chosen to illustrate the predictive power of this variable. It is found (Table 4) that z-values for filled blends decrease slightly with increasing filler content left and right to the maximum G'_{extra}. The smaller z the larger the predicted shift of the phase inversion concentration to higher concentrations of PMMA-phase for a given viscosity ratio. From Fig. 7 it can be recognized that the phase inversion concentration for the filled blends is well above the value for the non-filled blends and is best described with the line $z = 2$ in agreement with the data given in Table 4.

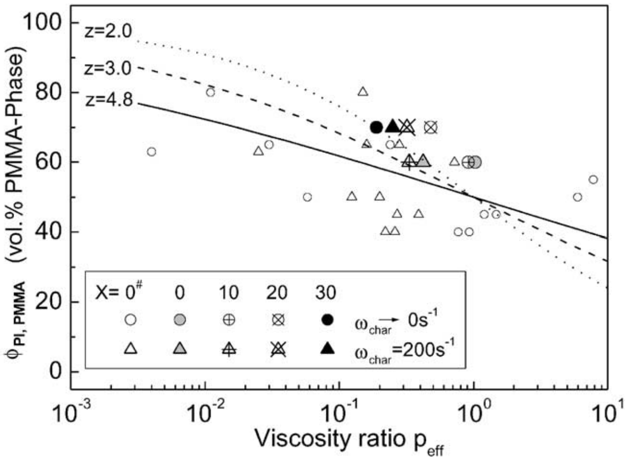

Fig. 7. Influence of the effective viscosity ratio at two extreme characteristic frequencies on the phase inversion concentration ϕ_{PI}. The data points at $\omega_{\mathrm{char}} \rightarrow 0\ \mathrm{s}^{-1}$ are represented by circular symbols and the triangular symbols stand for the data at $\omega_{\mathrm{char}} = 200\ \mathrm{s}^{-1}$. X denotes the Monosphere content in vol% and the index # marks the group of 11 non-filled series [13] excluding series B12Mono0 drawn with gray circles. The lines represent Eq. (10) for different z-values: $z = 4.8$ (full line), $z = 3$ (dashed line) and $z = 2$ (dotted line).

We conclude that the filled blends correspond to a z-value around 2 which is significantly different from what is known for the non-filled blends. Moreover, we have shown that selective filling does not change the mechanisms which are responsible for the position of ϕ_{PI}. This explains why we observe a regular shifting of ϕ_{PI} as predicted by theory derived for non-filled blends.

3.5. Stabilization of the cocontinuous morphology: the CCI

The cocontinuous morphology is a non-equilibrium morphology, which, once created during processing, disintegrates with time after the cessation of flow. A cocontinous morphology can be found in the prepared samples if the breakup time of the elongated interconnected domains is much shorter than a characteristic quench time.

Due to the fact that breakup time also depends on the size of the filaments those cocontinuous structures which are formed at the lowest possible content of minority phase are the thinnest and therefore destroyed fastest. As a consequence the cocontinuous morphology is observed in a much smaller composition range than primarily created during mixing. Additional parameters influencing the kinetics of fibril breakup are interfacial tension and matrix viscosity or elasticity (due to the coupling between viscosity and elasticity). The larger these parameters are the longer is the breakup time. As a result, the observed widening of the CCI upon filling can be explained by the slow down of all relaxation processes associated with the destruction of cocontinuity, such as fibril breakup due to the strong increase of melt viscosity and elasticity of the selectively filled PMMA-phase at zero shear rate conditions.

Coalescence as a further relaxation process is probably slowed down as well by filling as Gubbels et al. [14] propose. However, coalescence does not destroy cocontinuity but only leads to a coarsening of the domains, whereas the type of morphology is preserved until very late stages. In our opinion the increased stability of the cocontinuous morphology can only be explained by the slowdown of a process which leads to the destruction of the morphology, i.e. a process like fibril breakup.

In order to verify this idea we have investigated the influence of selective filler on fibril breakup in so-called Tomotika experiments [30]. Fibers of the unfilled and filled PMMA embedded in PS were microscopically observed during annealing at 200 °C. Here we give a short summary of the results, which will be presented elsewhere (Steinmann et al. [31]). We found that the fibril breakup of the PMMA-phase is slowed down dramatically by the addition of filler to this phase. While the growth rate of the disturbance amplitude of the fibril decreases from 8.9×10^{-4} to $2.5 \times 10^{-5}\ \mathrm{s}^{-1}$ upon addition of 10 vol% Monospheres, no breakup could be observed during annealing for 2 days in case of a monosphere-content of 30 vol%. This substantiates our conclusion that the observed widening of the CCI at both sides of the concentration window is caused by a slowdown of breakup.

4. Conclusions

Our strategy to use a selective filler to keep the rheological properties of the filled phase in the blend constant, makes it possible to discuss morphological and rheological changes caused by the addition of filler on a quantitative basis.

We have shown that the recently established rheological criterion for quantitative determination of the phase inversion concentration which is based on the analysis of blends' extra elasticity is also applicable to filled blends. Rheology has proved to be capable of differentiating between filler effects and morphological effects. Moreover, the results point out the relevancy of the elastic properties for the correlation between rheology and morphology.

Our investigations have also shown that zero shear properties of the blend components have very little influence on morphology development during melt processing in contrast to the impact of the rheological properties under higher shear rates. The characteristic $p-\psi$-correlation is not influenced by selective filling at higher shear rates, which are predominant in the extruder. This explains why we only detect a regular shift of the phase inversion concentration to higher concentrations of filled PMMA with increasing filler content, as predicted by theory.

The most important result of our work is that the addition of filler increases the stability of the cocontinuous morphology, leading to broadening of the cocontinuity interval. We explain this stabilization by a strong slowdown of destructive processes like fibril breakup by filling. Tomotika experiments confirmed this finding.

By the addition of a selective filler a fine tuning of morphology is possible and the cocontinuous morphology is accessible over a wider range of concentrations. Moreover, the cocontinuous blends are stabilized against post thermal treatment.

We conclude that selective filling is a way to control and to stabilize the morphology of immiscible polymer blends.

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