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Morphological and rheological detection of the phase inversion of PMMA/PS polymer blends

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SUMMARY

The phase inversion process was investigated from different points of view. First, a reliable on-line and off-line method of morphology detection using light microscopy is established. The method provides fast information that can be used to discriminate between different types of morphologies.
Second, TEM images are modelled with Markov Random Fields. For characterization purposes image features are introduced and tested. A combination of features allows classification of different morphologies of PMMA/PS blends.
In the third part we show that the rheological properties of blends allow also discrimination between different morphologies.

INTRODUCTION

Most polymer blends consist of a matrix, in which a second component is dispersed. Gradually increasing the concentration, ϕ_2, of this component the phase inversion occurs. Both phases are continuous at this transition point and the corresponding concentration is called phase inversion concentration, ϕ_{2I} (1). Such cocontinuous blends are also called interpenetrating polymer blends, IPB. IPB have the advantage of being produced by simple mechanical mixing with no need for chemical modification (2). Due to this special morphology these blends can have favorable properties like improved impact strength. However, there is a lack in theoretical understanding of the underlying processes and the kind and number of parameters controlling the phase inversion (3), (4).
It is the aim of our paper to detect and to characterize the phase inversion for PS/PMMA polymer blend as a model system. In the first part a combination of a flat sheet die of a laboratory extruder with a light microscope is introduced. In the second part two-dimensional TEM images are analyzed to characterize the inversion point. Both methods are tested for their characterization capabilities. The third part describes, how the rheological properties of the blends can be used to differentiate between the various morphologies and how the addition of block copolymers (5) changes the rheological properties and stabilizes the morphology.

EXPERIMENTAL

Materials

Polystyrene (PS) and poly(methyl methacrylate) (PMMA) are used as blend components. Their molecular weights M_w, and M_n, as well as polydispersity index (PD) are given in

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Table 1. Within this paper we will concentrate on two compositions: ϕ_2 = 30% PMMA representing the spherical morphology and ϕ_2 = 50% PMMA, a cocontinuous morphology.

The block copolymer used as compatibilizing agent has a molecular weight of M_w = 108.000g/mol and a polydispersity index of 0.1. The molecular weights of the PS and PMMA blocks are 53.000 g/mol and 55.000 g/mol, respectively. Details of its characterization are given elsewhere (6). To ensure a constant PS to PMMA ratio during compatibilisation, the weight fractions of the homopolymers were reduced accordingly.

Table 1: *Molecular weights and the polydispersity index of the homo-polymers*

Polymer	M_w	M_n	PD
	g/mol	g/mol	-
PS	99300	96400	0.03
PMMA	29000	26100	0.11

Extrusion

The powder of the homopolymers was premixed in a mixer for 30 min. 5 g of the blends were given into the hopper of a Randcastle Microtruder RCP MT 0250. The temperature profile along the screw changes from 200°C at the entrance to 220°C at the die. The polymer blend was directly extruded with a screw speed of 30 rpm into a preheated (220°C) cylindrical mold (diameter of 25 mm and a height of 1.3 mm). For on-line microscopy a specially designed flat sheet die with variable slit height equipped with an optical window (2 plates of Spektrosil B, MGT) was used. A slit height of 0.2 mm was used in the following experiments.

Light microscopy

The light beam (Highlight 3001, Olympus) passed the window of the die perpendicular to the extrusion direction, the microscope being positioned on the opposite side. A long working distance objective (Olympus) allowed a required distance of about 5 mm between the heated die and the objective. The coupling of the microscope with a CCD camera (CF 8/1 DXC, Kappa) and a computer allows to take very fast (20 ms) digital images (software DX control, Kappa) during the experiment. The software offers the possibility to calibrate the dimensions of the digital images with microscope tools (objective micrometer with 10 µm distance, Möller GmbH), which allows quantitative evaluations of the images. In case of on-line detection the screw speed was reduced (5 rpm) in order to take images with sufficient sharpness.

Transmission Electron Microscopy (TEM)

Ultrathin cuts were made on a Leica Ultracut-E microtome with a diamond knife. The thickness of the sections was about 60 nm. TEM elastic bright field images were taken on a Zeiss CEM 902, operating at 80 kV, with monoenergetic electrons (ESI mode). The morphologies of the blends were analyzed using the image processing system SIS.

Rheology

Rheological measurements were carried out with a CVO rheometer (Bohlin) in parallel-plate geometry (plate diameter of 25mm). Frequency sweeps (100-0.1 rad/s) were recorded between 150°C and 200°C in steps of 10 degrees. The reference temperature was 180°C. All measurements were made under a N_2 atmosphere to avoid decomposition.

RESULTS and DISCUSSION

Detection of the phase inversion with light microscopy

On-line images during extrusion can be taken in the range of concentrations up to 30%. Figure 1 shows such an on-line image for the composition of 30% PMMA where only spheres are observed. For large ϕ_2 the turbidity of the samples caused by strong light scattering and the poor sharpness caused by motion of a large number of particles with complex form prevent an on-line detection of morphology at the moment. Nevertheless, the dimensions of the domains can be estimated in an off-line experiment, in which a piece of the extrudate is placed between the light source and the objective of the microscope without any disturbing glass window. The advantage of this off-line experiment is, that the particles are fixed and can be focused more precisely. Figure 2 shows such an off-line image of a blend with the composition of 50% PMMA.

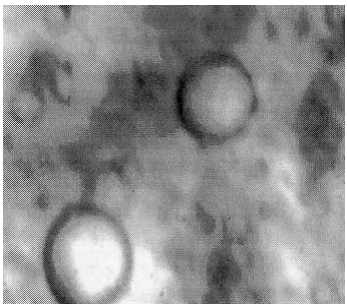

Figure 1*: On-line image during the extrusion of a blend with 30% PMMA in PS. The presented image has the dimension of 65.6 µm x 50.9 µm.*

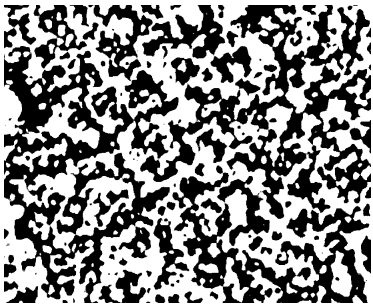

Figure 2: *Off-line binary image from a blend with 50% PMMA. The presented image has the dimension of 65.6 µm* x *50.9 µm.*

We have already shown that there are no significant differences between measured particle sizes determined from the on-line or the off-line experiment (7). The corresponding analysis concerning the dimensions of domains in blends with cocontinuous morphology is still missing.

For blend sizes on a µm scale and low speed of the extruder screw on-line measurements with the combined microscope are very fast and easy. It is possible to record the flow - induced structure in situ and avoid the time consuming TEM techniques.

Modelling and Characterization of the phase inversion process

Morphologies of polymer blends can be interpreted as realizations of Markov Random Fields (MRF) (8). This is motivated by some similarity to ferromagnetic matter, which is described by the Ising Model, a special kind of MRF (9). Ferromagnetic matter builds randomly distributed domains with a finite magnetization just as polymer blends form domains of each polymer.

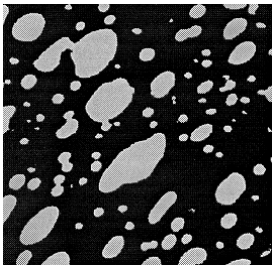

Figure 3a: *TEM image of 30% PMMA in PS*

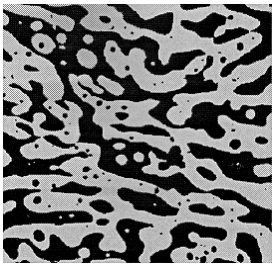

Figure 3b*: TEM image of 50% PMMA and 50% PS*

Within this model a random field $\vec{h}$ is introduced, where the value of the components $h_i \equiv h(\vec{x}_1)$ is equal to +1, if PMMA is at the point $\vec{x}_i$ and equal to -1 if PS is at $\vec{x}_i$, (i = 1,…, $N_x \cdot N_y$). The size N_x and N_y, respectively, of the image is usually given in 'pixels' and is typically of the order of 500. The size of the pixel represents a lower limit for a characteristic length scale which is negligible in comparison to the length scale of morphology. Therefore, the real morphologies can be compared to the simulated images.

One ansatz for the probability distribution p of the random field $\vec{h}$ is

$$p(\vec{h}) \propto \exp\left\{-\beta \sum_{i=1}^{N_x \cdot N_y} h_i \, f(h_i)\right\} \quad \text{with} \quad f(h_i) = \sum_{i' \in \mathcal{N}_i} h_{i'} \tag{1}$$

where $\mathcal{N}_i$ is a suitably defined neighbourhood of x_i and β is a measure for the interactions between neighbouring sites.

The magnetization which in our considerations is equivalent to the difference of the weight fractions, ϕ_2-ϕ_1, is not adjustable in this model. For that reason it is necessary to modify the model by taking into account the additional constraint that ϕ_2 is fixed. This model is known in literature as Modified Ising Model (10).

Typical configurations of the random field $\vec{h}$ can be generated with an Exchange Algorithm (11) which is a modification of the Metropolis Algorithm (12). Such configurations with ϕ_2 equal to 30 % and 50 % are shown in figure 4.

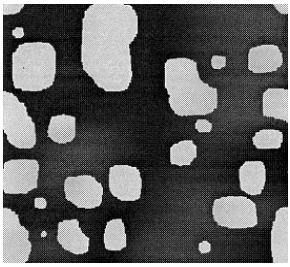

Figure 4a: Simulation for ϕ_2 =0.3 and β = 1.5

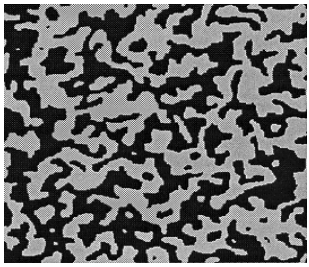

Figure 4b*: Simulation for* ϕ_2 = 0.5 and β = 1.5

Thus, the Modified Ising Model is able to generate two dimensional images or, in other words, morphologies which look like the experimental data. Moreover, because the characteristics of phase transitions depend on the dimension, one expects to obtain even more realistic images from simulations in three dimensions. Then, the dependence of the model parameters β and ϕ_2 on the morphology will be investigated. Moreover, we will look for a possible relationship between β and the rheological properties.

In order to characterise morphologies typical. features as e.g. the ratio of area to length of the interface have to be considered. It is reasonable to assume, that these features depend on the interfacial tension which can be correlated to local interactions described with the parameter β of the MRF.
In order to describe the interface a random variable $\vec{u} = (u_1,...u_{Nx \cdot Ny})$ with

$$u_i = h(\vec{x}_i) - h(\vec{x}_i + \vec{\delta}) \qquad (2)$$

is introduced for some $\vec{\delta}$. As feature components the moments or the entropy of the distribution function of $\vec{u}$ are considered where, as usual, the entropy of $\vec{u}$ is the logarithm of its distribution function.
Other approaches are the determination of the form factor (13), the domain area, and concepts of fractal dimensions (14) or overlapping areas (15). A comparison of these features shows that entropy and domain area are the best features to distinguish between the spherical and the cocontinuous morphology. Figure 5 shows the entropy and the form factor of PMMA/PS blends. The entropy allows better characterization.

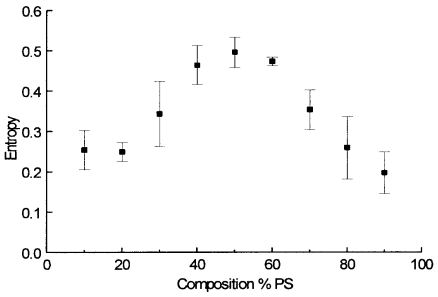

Figure 5a. *Entropy in dependence on the composition*

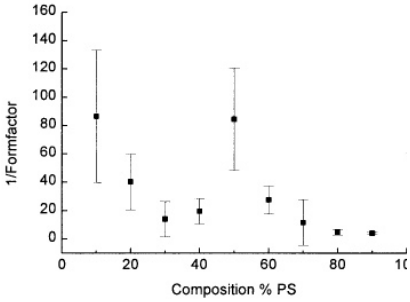

Figure 5b. *Form factor in dependence on the composition*

Investigations of PMMA/PS blends with a cocontinuous morphology where block copolymers are added have shown that the feature 'entropy' is the best discriminator. A combination of features into a feature vector gives a complete description of the typical morphological characteristics.

Detection of the phase inversion via rheology
Here we will compare the different rheological responses of polymer blends with spherical and cocontinuous morphologies. It is known from literature that for blends with spherical morphology there is an additional contribution to the storage modulus, G', in the range of low frequencies (16,17,18). This contribution is attributed to relaxation of the shape of ellipsoidal deformed particles back to spheres and is presented in Figure 6 where the master curves are given for G' and the loss modulus, G", of the blend containing PMMA 30%. The form relaxation process carries all information about the sphere size distribution and the interfacial properties. This information cannot be derived from the measurements due to a missing rheological model that characterizes the particles

interactions in a quantitative correct way. The scatter in the G' data at small frequencies can be explained by slight changes in the spherical morphology which is not stabilized in this case by block copolymers. Nevertheless, the corresponding form relaxation time can be determined calculating the relaxation time spectrum with a nonlinear regularization method (19). The form relaxation time of this sample is 130 s.

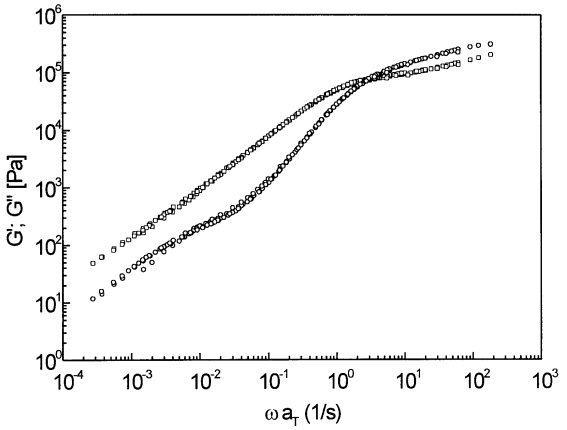

***Figure 6**: Shear storage modulus G'(ω) (○) and shear loss modulus G''(ω) (□) of the blend PS 70% and PMMA 30%, T_{ref} = 180°C*

In the case of dual phase continuity the rheological response changes significantly. The elasticity is reduced and the form relaxation shoulder disappears (see Fig. 7, curve a)). The data points measured at lower frequencies indicate power law like relaxation. Such behavior is characterized by the following relation: $G' \propto \omega^{\alpha}$ with $\alpha < 1$. This is reasonable because the presence of domains with different characteristic length scales generates relaxation processes with different characteristic times. This seems to be the new feature in the rheological response of polymer blends with phase cocontinuity.

TEM images taken at different stages of rheological experiment give evidence of coalescence. This process can be stopped by adding block copolymers. The addition of block copolymers changes the dynamic moduli significantly as can be seen from Figs 7b and 7c. In the range of high frequencies the elasticity of the blend decreases whereas at small frequencies a strong increase is observed. The power law character of relaxation is not changed. This strong dependence of the rheological response on the amount of added compatibilizing agent opens the possibility to discriminate also between different degrees of cocontinuity as it can be observed from TEM.

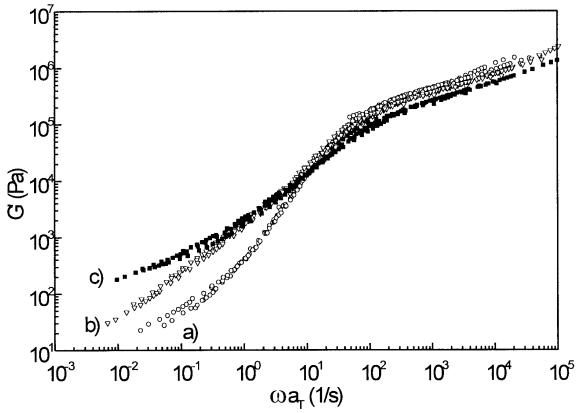

***Figure 7**: Shear storage modulus G' (ω) of a) PS 50% PMMA 50%, b) with 5% block copolymer and c) with 10 % block copolymer, T_{ref} = 180°C*

By calculating the relaxation time spectra it is not possible to determine a terminal relaxation time. Blends with cocontinuous morphologies do not flow at least in this range of frequencies. This

fact is in accordance with interpenetrating phase structure observed by TEM and light microscopy.

CONCLUSIONS

Combining the flat sheet die of a laboratory extruder with a light microscope a fast and reliable detection of the flow induced morphology of polymer blends is possible in the concentration range up to 30 % of the minor component. For higher concentrations the on-line measurements are difficult due to intense light scattering. Nevertheless, if the domain size in the blend is in µm scale an off-line experiment helps to record the morphology without complicated sample preparation.

Morphologies of PS-PMMA blends can be modeled by MRF using an Exchange Algorithm. A combination of the features ‘entropy’ and ‘domain size’ gives a feature vector which allows the discrimination of morphologies with different degrees of cocontinuity.

The sphere morphology exhibits an additional contribution in the range of low frequencies attributed to the relaxation of particles. In the case of cocontinuity, the morphology can be stabilized using a compatibilizer and the degree of cocontinuity increases. Those blends do not flow in this frequency region, no terminal relaxation time can be calculated due to their interpenetrating morphology.

LITERATURE

1. Mekhilef N, Verhoogt H (1996) Polymer 37:4069
2. Miles I, Zurek A (1988) Polymer Eng Sci 28:796
3. Wu SH (1987) Polymer Eng Sci 27:335
4. Utracki LA (1991) J Rheol 35:1615
5. Harrats C, Blacher S, Fayt R, Jerome R, Tessie Ph (1995) J Polym Sci Part B 33:801
6. Riemann R-E (1997) PhD-Thesis Freiburg
7. Leukel J, Weis C, Friedrich Chr, Gronski W (1997) Polym Comm submitted
8. Li Z (1986) Markov Random Fields in Computer Vision Imaging Image Analysis. Springer, Tokio
9. Onsager L (1944) Phys Rev 65:117
10. Winkler G (1995) Image Analysis, Random Fields and Dynamic Monte-Carlo-Methods. Springer, Berlin
11. Cross GR (1983) IEEE Trans Pattern Anal Machine Instell 5:1
12. Metropolis N, Rosenbluth AW, Rosenbluth MN, Teller AH, Teller E (1956) J Chem Phys 21:1087
13. Rosenfeld A, Kak C (1993) Digital Picture Processing. Academic, San Diego
14. Ruffier M, Vincent N (1993) Polym Bull 30:111
15. Heeschen WA (1995) Polymer 36:1835
16. Gramespacher H-J, Meissner J (1992) J Rheol 36:1127
17. Graebling D, Muller R, Palierne JF (1993) Macromolecules 26:320
18. Friedrich Chr, Gleinser W, Korat E, Maier D, Weese J (1995) J Rheol 36:1411
19. Honerkamp J, Weese J (1993) Rheol Acta 32:65