

# Morphological and Rheological Properties of PS Melts Filled with Grafted and Ungrafted Glass Beads

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## SYNOPSIS

Glass beads carrying different amounts of polystyrene (PS) grafted to their surface were prepared by solution and melt-mixing processes. These beads are mixed with a nearly mono-disperse PS. The morphology of polymers filled with different volume amounts,  $\Phi$ , of modified and unmodified glass beads was investigated by scanning electron microscopy (SEM). In the case of PS-grafted glass beads, the fracture surfaces show cohesive failure. The rheological properties of these filled polymers were investigated by mechanical spectroscopy. The material functions, the storage modulus  $G'$  and the loss modulus  $G''$ , for PS melts filled with unmodified beads can be presented in an invariant form, i.e., independent of temperature and concentration. The temperature-shift factors follow WLF behavior, and the concentration shift factors a generalized Maron Pierce equation. The rheological material functions of melts filled with modified glass beads can be superposed for different temperatures. However, a concentration invariant representation is only possible in the frequency range belonging to the plateau region. For small frequencies, a systematic deviation occurs whose strength depends on the amount of polymer grafted to the filler surface. It is argued that this behavior may be attributed to an additional relaxation process originating from the hindered flow of the modified glass beads. This process has to be investigated in more detail in the future. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

Fillers are used extensively to improve the mechanical properties of polymeric matrix resins. Stiffness, strength, hardness, and abrasion resistance are usually increased with increasing amounts of fillers.<sup>1</sup> Addition of fillers to polymers also alters their flow behavior and thus processability. Generally, upon filling, the viscosity of the composites is increased and yield stresses may develop.<sup>2</sup> The influence of filling on the rheological behavior of composites is well understood from the experimental as well as from the theoretical point of view in the range of small concentrations. In the range of higher concentrations, the straightforward solution of hydrodynamic equations is difficult and only approximate solutions

or numerical results are available. For the highest concentrations where direct contacts between the particles dominate the flow behavior, the theoretical description is based on empirical models. Formulas originating from percolation theory have been widely used during the last decade.

The main subjects of the rheology of composites are investigations of the influences of the rheological properties of the matrix and of the mechanical properties of the fillers on the properties of the composite. In a series of review articles,<sup>3-5</sup> the most relevant factors have been analyzed. However, only little attention has been paid to the contributions of an interfacial shell around the filler particles, although flow properties strongly depend on the interfacial conditions. Adhesion phenomena as well as the interaction between matrix polymer and covalently grafted polymers on the filler surface are of importance. Maurer and co-workers<sup>6,7</sup> report on the remarkable influence of a covalently bonded polymer shell on the dynamic moduli of a glass bead-filled

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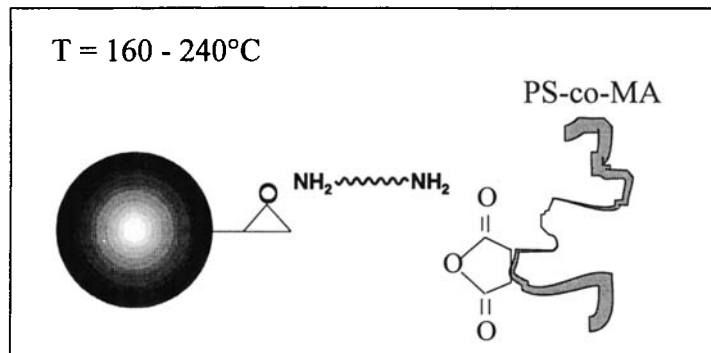


Figure 1 Reaction scheme.

polyethylene. The rheological curves are shifted to higher moduli for composites filled with modified glass beads compared with composites filled with nonmodified glass beads. This increase of the modulus is also observed in the solid-state properties and one may speculate that it is due to the same mechanism. However, conclusions about possible additional relaxational processes caused by the presence of an interlayer or by enhanced particle-particle interactions leading to an equilibrium modulus,  $G_e$ , cannot be derived from these data. This may be a consequence of the high polydispersity of the matrix.

Nevertheless, it is well accepted that adhesion phenomena between the polymer and filler surface play an important role in this respect. For example, the work done by Macosko and co-workers<sup>8</sup> shows that rheological properties depend on the

concentration of silanol groups on the surface and on the molecular weight of the matrix polymer. Although the particles used in their investigation were small in size and large in specific interface, the possible appearance of an equilibrium modulus was smeared out by the use of polydisperse matrix resins.

It was the aim of this article to compare the rheological properties of polystyrene (PS) melts filled with glass beads carrying grafted polymers on the surface (compatibilized beads) with those where the glass beads are "clean." To obtain the greatest possible amount of information, the matrix PS is of high molecular uniformity to investigate the differences between the two systems in more detail. We explore the morphology and rheology of these composites and judge how sensitive the rheology of these materials depends on

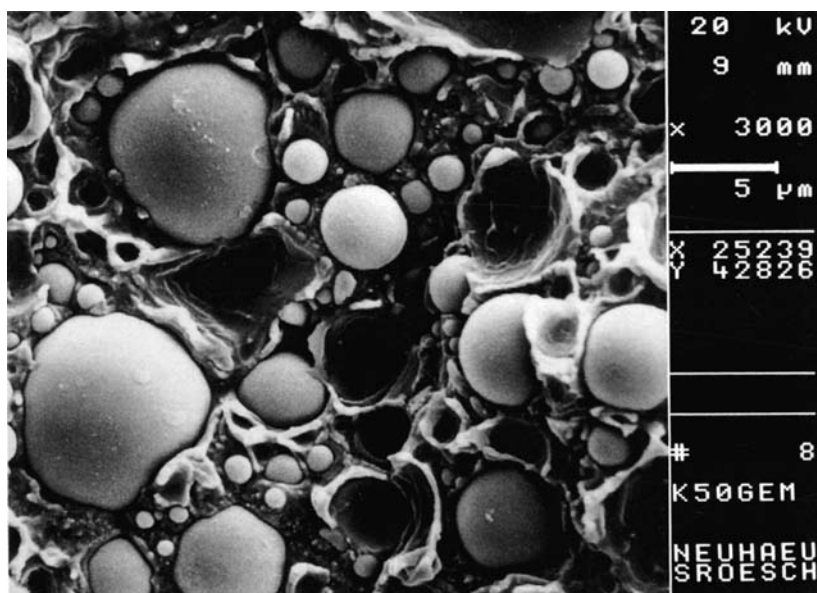
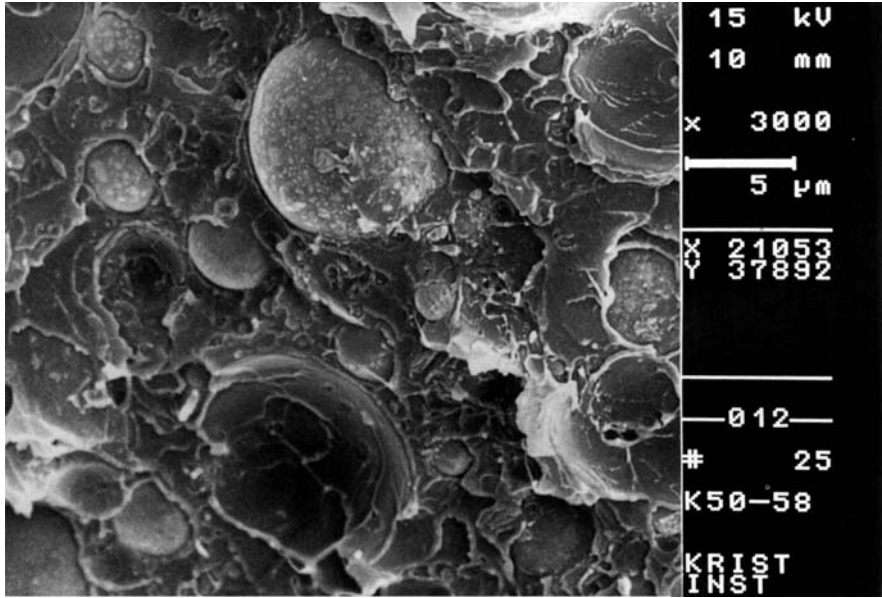
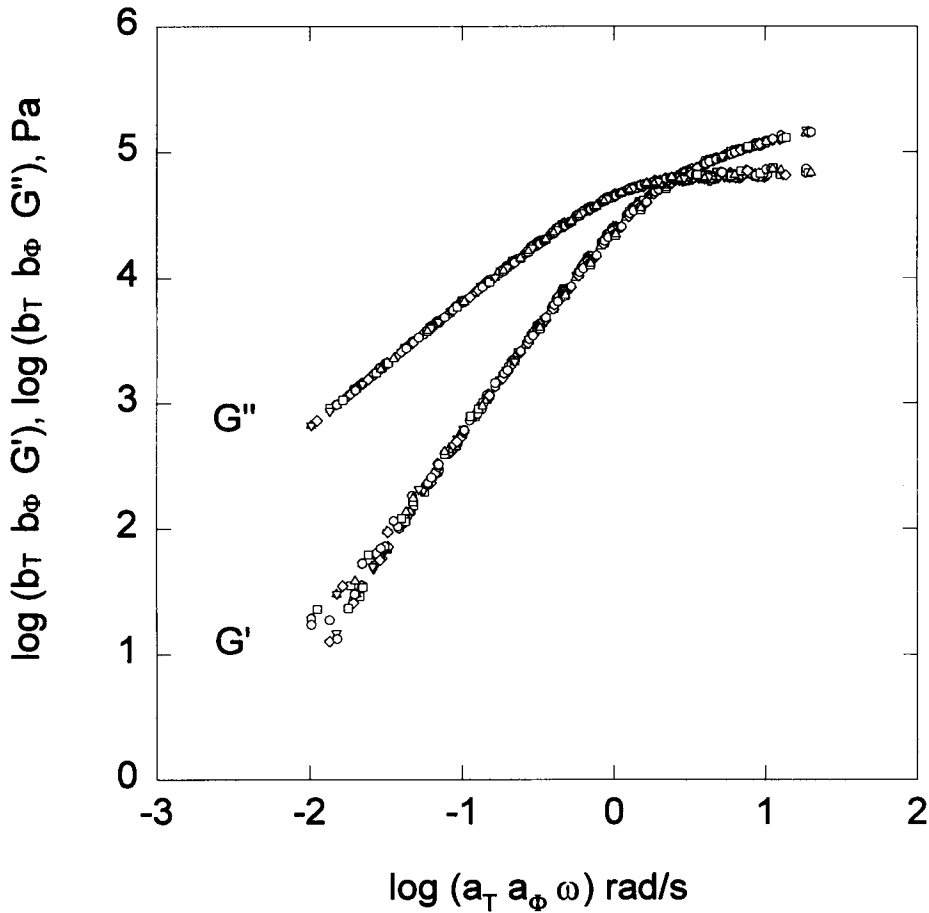


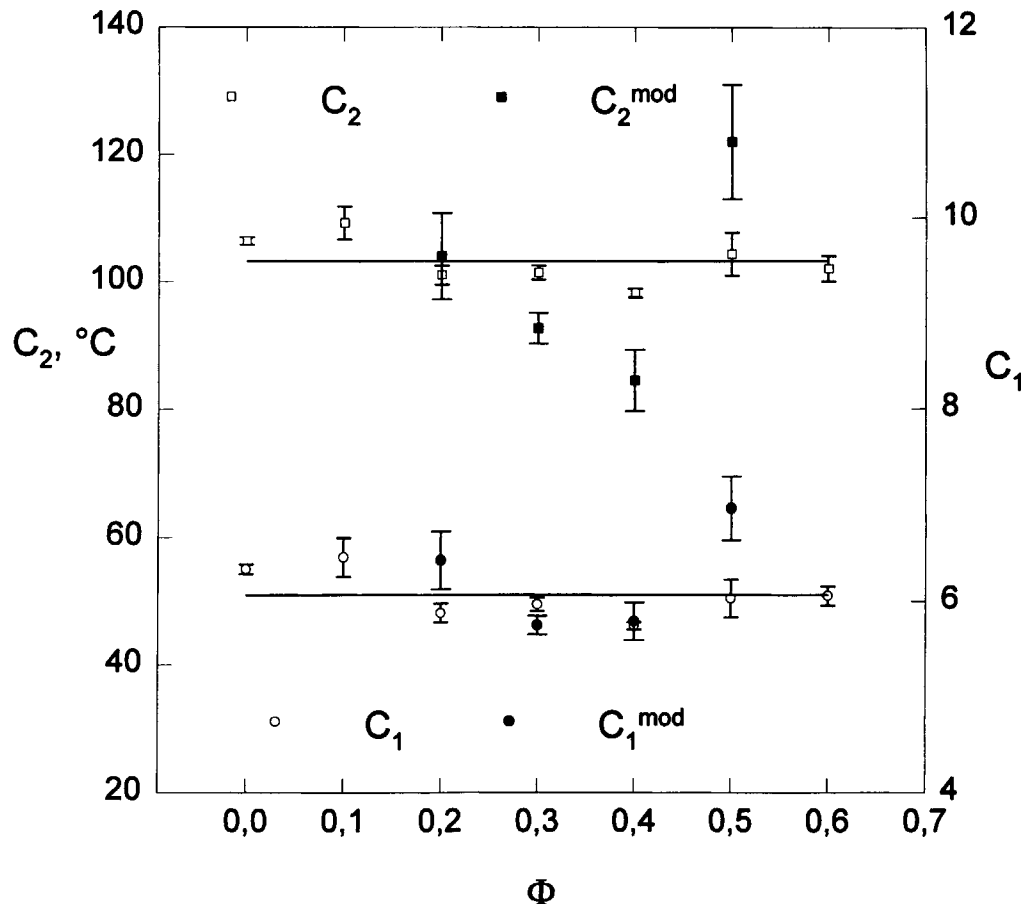
Figure 2 SEM image of PS filled with 50 vol % of ungrafted ("clean") glass beads.



**Figure 3** SEM image of PS filled with 50 vol % of polymer-grafted (“compatibilized”) glass beads ( $\Phi_{gr} = 12$  wt %).



**Figure 4** Concentration and temperature-invariant presentation of the loss modulus,  $b_T b_\phi G''$ , and storage modulus,  $b_T b_\phi G'$ , in dependence on the generalized frequency,  $a_T a_\phi \omega$ , for PS filled with ungrafted glass beads.



**Figure 5** Dependence of the WLF parameters  $C_1$  and  $C_2$  on the degree of filling,  $\Phi$ . The open symbols correspond to the ungrafted ("clean"), and the filled symbols, to the grafted ("compatibilized") glass beads.

the amount of polymer bonded on the surface of the glass beads.

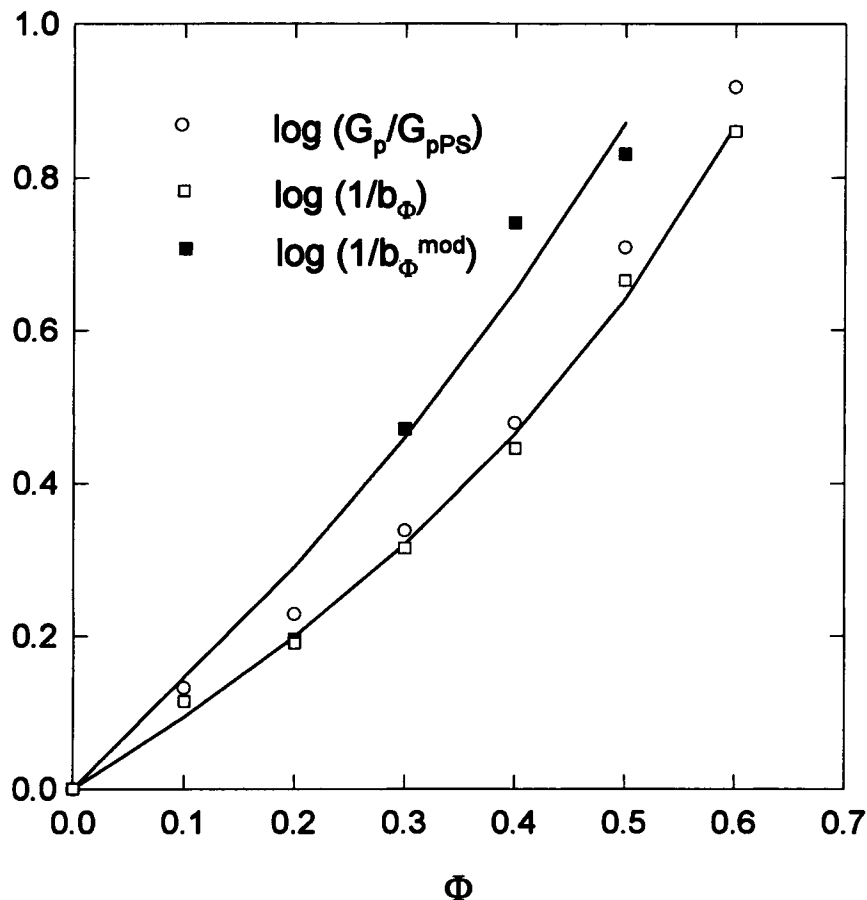
## EXPERIMENTAL

For our investigations, we used a monodisperse polystyrene PS100 ( $M_w = 96$  kg/mol,  $U = 0.08$ , GPC [Chloroform, PS-standards]) as the matrix material, which was supplied by BASF. As fillers not interacting with the matrix, aminosilane-treated glass beads (Potters Ballotini G 5000 CP0320, median diameter  $10 \mu\text{m}$ ,  $0.2$  wt % aminosilane) were used. These glass beads are perfectly spherical in shape, and the rheological behavior is therefore unaffected by particle anisotropy or particle-network formation. The treatment with silane assists dispersion in the matrix resin.

Grafted fillers were prepared from glass beads of the same size and size distribution. Instead of ami-

nosilanes, the particle surface is modified with  $0.2$  wt % epoxysilane. Grafting was achieved by reaction with poly(styrene-*co*-maleic anhydride) (SMA) via a diamine spacer (1,6-hexanediamine). SMA ( $M_w = 316$  kg/mol,  $U = 0.81$ , MA concentration:  $5.8$  wt %) was supplied by BASF. The grafting reaction—the reaction scheme is presented in Figure 1—was carried out in solution or in melt under various conditions to ensure different degrees of grafting. The degree of grafting,  $\Phi_{gr}$ , was checked by thermogravimetric analysis using a Netzsch STA 409 C TGA instrument.

All composites were prepared under identical mixing and molding conditions. Filler volume fractions,  $\Phi$ , were varied from  $0$  to  $60$  vol % in the case of clean fillers and from  $0$  to  $50$  vol % in the case of compatibilized fillers. Melt blending was performed in a Haake Rheomix 90 equipped with a  $60$  mL mixing chamber that had been preheated to  $200^\circ\text{C}$ . The appropriate polymer-filler mixtures,



**Figure 6** Dependence of the relative plateau modulus,  $G_p/G_{pPS}$ , and the vertical concentration shift factor,  $b_\Phi$ , on the degree of filling,  $\Phi$ . The open symbols correspond to the ungrafted, and the filled symbols, to the grafted glass beads. The lines correspond to eq. (1).

including 0.2 g antioxidant (80% Irganox 1010/20% Irgafos 168 [Ciba Geigy]), were kneaded for 6 min at 60 rpm. The temperature was checked by a thermocouple placed in the wall of the mixer. After mixing, the blend was quickly removed and cooled. Sheets of 1.5 mm thickness were prepared by compression molding in an evacuated press (Schwabenthal Polystat 100) after annealing at 200°C for 20 min and quenching to room temperature between water-cooled metal plates. Disks of 20 mm diameter were cut out of these plates and dried at 70°C under vacuum before testing.

The morphology of the blends was determined by SEM. The fracture surfaces sputtered with gold were investigated using an electron microscope DSM 960 from Zeiss.

The rheological material functions  $G'$ , the storage modulus, and  $G''$ , the loss modulus, were determined in dependence on the frequency  $\omega$  and temperature  $T$  on a Rheometrics RMS 800 rheometer. Strain sweep

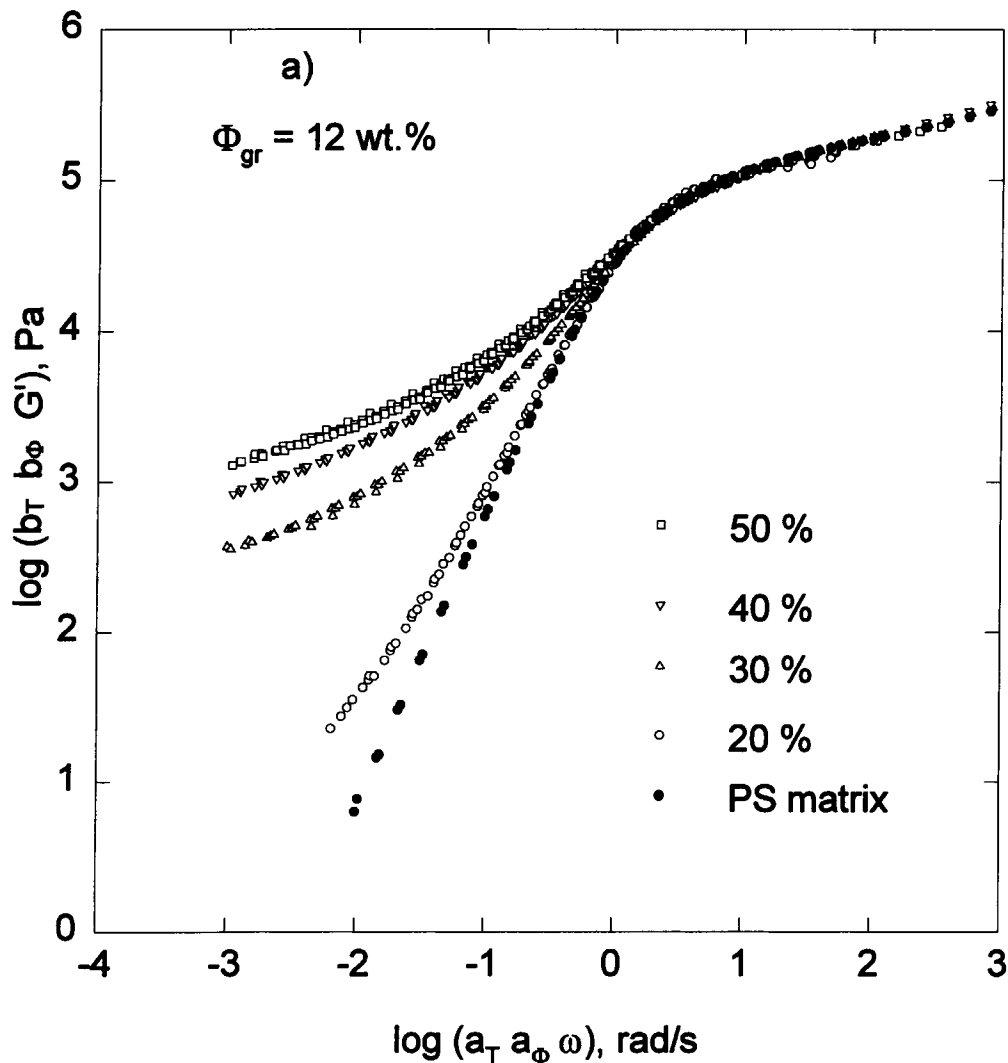
experiments confirmed that amplitudes within 10% for low-volume fractions and of about 1% for higher-filler volume fractions remained within the limits of linear viscoelastic behavior. Time sweeps at the highest temperatures were performed to ensure that no chemical modification occurs.

We constructed master curves for the temperature interval under investigation (160–240°C) from the isotherms, and later on, master curves for the concentration  $\Phi$  from the temperature master curves. In all cases, the reference temperature was  $T_{\text{ref}} = 170^\circ\text{C}$  and the reference concentration  $\Phi_{\text{ref}} = 0\%$ . The shift program that we used was developed by Weese.<sup>9</sup>

## RESULTS

### Morphology

Figures 2 and 3 show SEM images of polystyrene filled with 50 wt % of clean and compatibilized glass



**Figure 7** Concentration and temperature-invariant presentation of the (a) storage modulus,  $b_T b_\phi G'$ , and (b) loss modulus,  $b_T b_\phi G''$ , in dependence on the generalized frequency,  $a_T a_\phi \omega$ , for the PS filled with different amounts,  $\Phi$ , of grafted glass beads.

beads, respectively. In the case of uncompatibilized beads, the fracture surface is along the interface. Obviously, no polymer (SMA) is bonded to the glass bead's surface. In the case of compatibilized glass beads, the fracture occurs within the matrix and we observe cohesive failure. The smallest glass beads are covered by matrix material and are no longer visible in the SEM picture.

#### Rheology of Melts Filled with Ungrafted ("Clean") Beads

Figure 4 shows the dynamic moduli of the melt filled with uncompatibilized glass beads in their temperature and concentration invariant form. This figure is the result of two sequential shift procedures: (1)

the temperature shift and (2) the concentration shift. It is seen from that figure that the characteristic relaxation regions are obtained for all temperatures and concentrations: the flow region for the lowest frequencies and the plateau region for the highest frequencies. Both regions are separated by a short transition which is characteristic for polymer matrices with small polydispersity.

The temperature shift factors,  $a_T$  and  $b_T$ , follow WLF behavior for all concentrations. The temperature variation leads only to a horizontal shift; thus,  $b_T$  is constant and equal to 1. In Figure 5, the WLF coefficients  $C_1$  and  $C_2$  are given in dependence on the concentration (open symbols). The values obtained are characteristic for monodisperse PS matrix material.

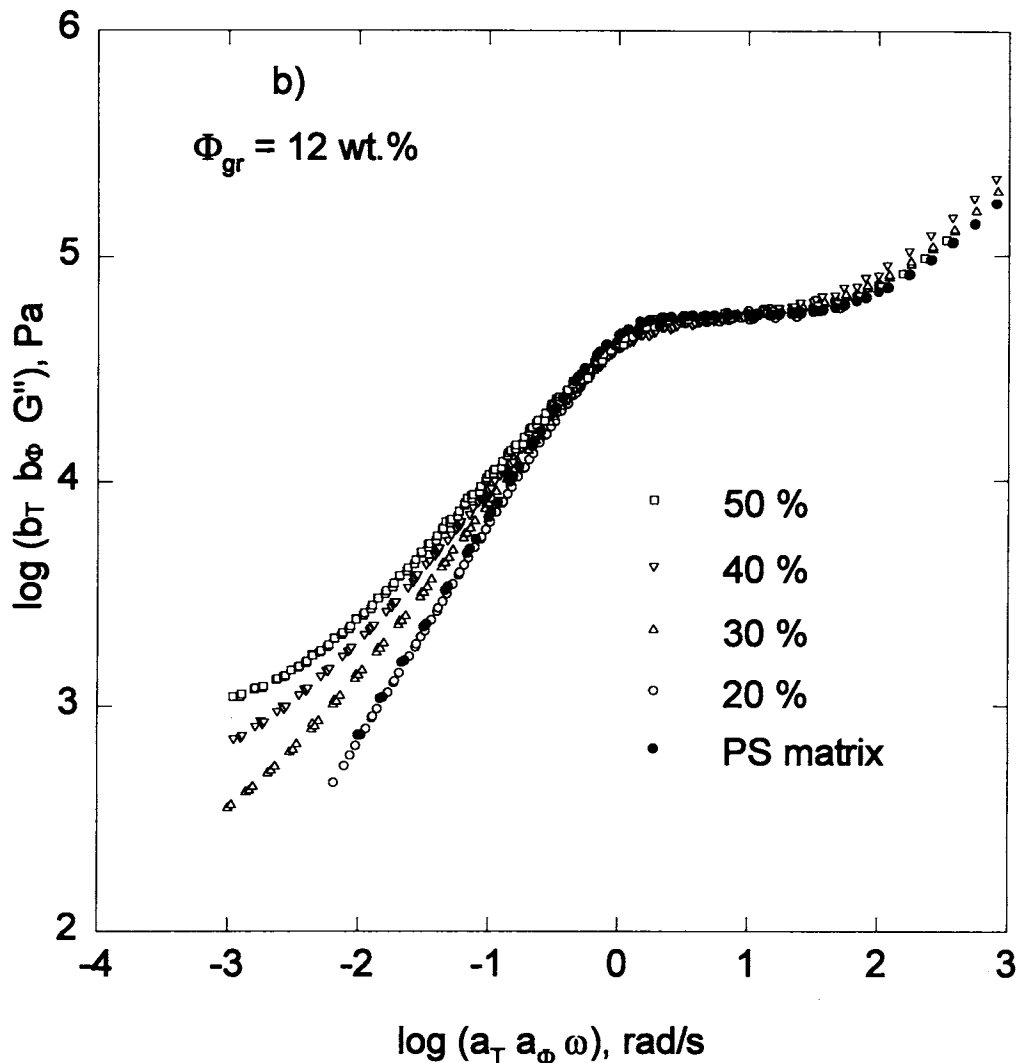


Figure 7 (continued)

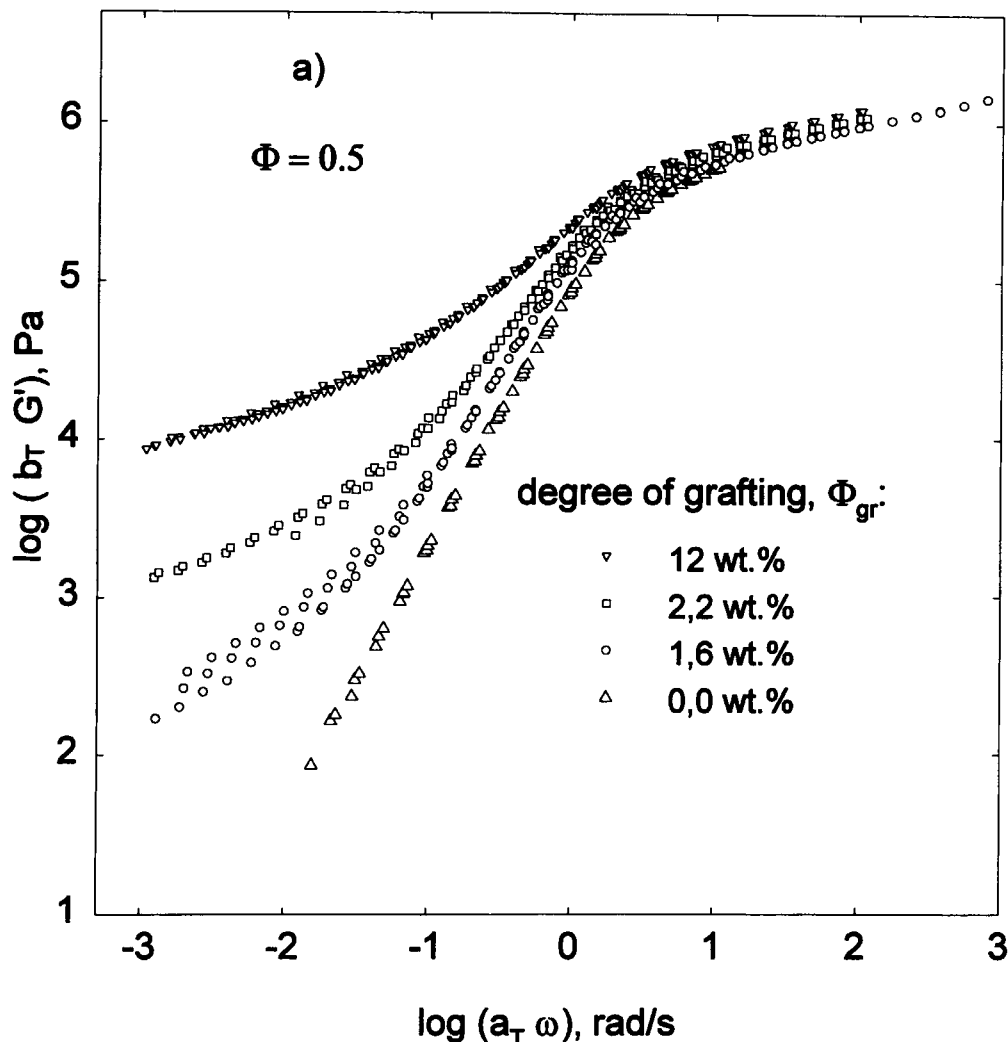
The different temperature-master curves were shifted to one by vertical shifting for the different concentrations. This shift is accounted for by the shift factors  $a_\phi$  and  $b_\phi$ . The shift factors  $b_\phi$  are given in Figure 6 by open squares. The logarithm of the inverse vertical shift factor  $b_\phi$  follows a nonlinear dependence on concentration, whereas the horizontal shift factor  $a_\phi$  is constant and nearly equal to 1. To show that the shift follows the concentration dependence of the plateau modulus, the latter is also given in normalized form (open circles).

**Rheology of Melts Filled with Polymer-grafted (Compatibilized) Beads**

In analogy to Figure 4, the dynamic moduli of the PS matrix containing compatibilized glass spheres

(degree of compatibilization  $\Phi_{gr} = 12$  wt %) in dependence on the temperature and concentration reduced frequency are given in Figure 7(a) and (b). The concentration shift was carried out to achieve coincidence of the data in the plateau region. The corresponding shift factors for the temperature shift and the concentration shift are given in Figures 5 and 6 by filled symbols.

To compare the rheological response of the composites filled with glass beads of different degrees of compatibilization at a given volume fraction (here, 50%), the corresponding data sets are presented in Figure 8(a) and (b). The curves show that the rheological behavior of these materials depends strongly on the amount of grafted polymer. Increasing amounts of surface-grafted polymer increase the moduli at low frequencies. These curves are not



**Figure 8** Comparison of (a) the temperature-invariant storage modulus,  $b_T G'$ , and (b) temperature invariant loss modulus,  $b_T G''$ , in dependence on the generalized frequency,  $a_T \omega$ , for the PS filled with grafted glass beads of different amounts of grafting,  $\Phi_{gr}$ . The degree of filling,  $\Phi$ , is 50%.

given in a concentration-invariant form. Thus, a small influence of the degree of grafting on the plateau modulus can be observed. This can also be recognized from Figure 6, where the shift factors for both curves are compared.

## DISCUSSION AND CONCLUSIONS

First of all, the importance of using monodisperse matrix material is discussed. Matrix resins with narrow molecular weight distributions show sharp transitions from the elastic to the flow region. This is essential for the investigations described above because the rheological effects due to filler-matrix

and filler-filler interactions occur in this transition region and might be smeared out by polydisperse matrix resins. This was the case in Maurer's experiments, where a nearly equidistant shift of the rheological curves to higher moduli was observed.

We used a PS matrix with a narrow molecular weight distribution as standard (reference) material. If this material is filled with clean glass beads, the rheological response can be derived from the rheological behavior of the matrix and some scaling relations. Filling with uncompatibilized beads leads to filler-filler interactions only for the highest degree of filling. A small but significant equilibrium modulus ( $G_e = 46$  Pa) occurs. This value was determined by fitting the data to an empirical model containing



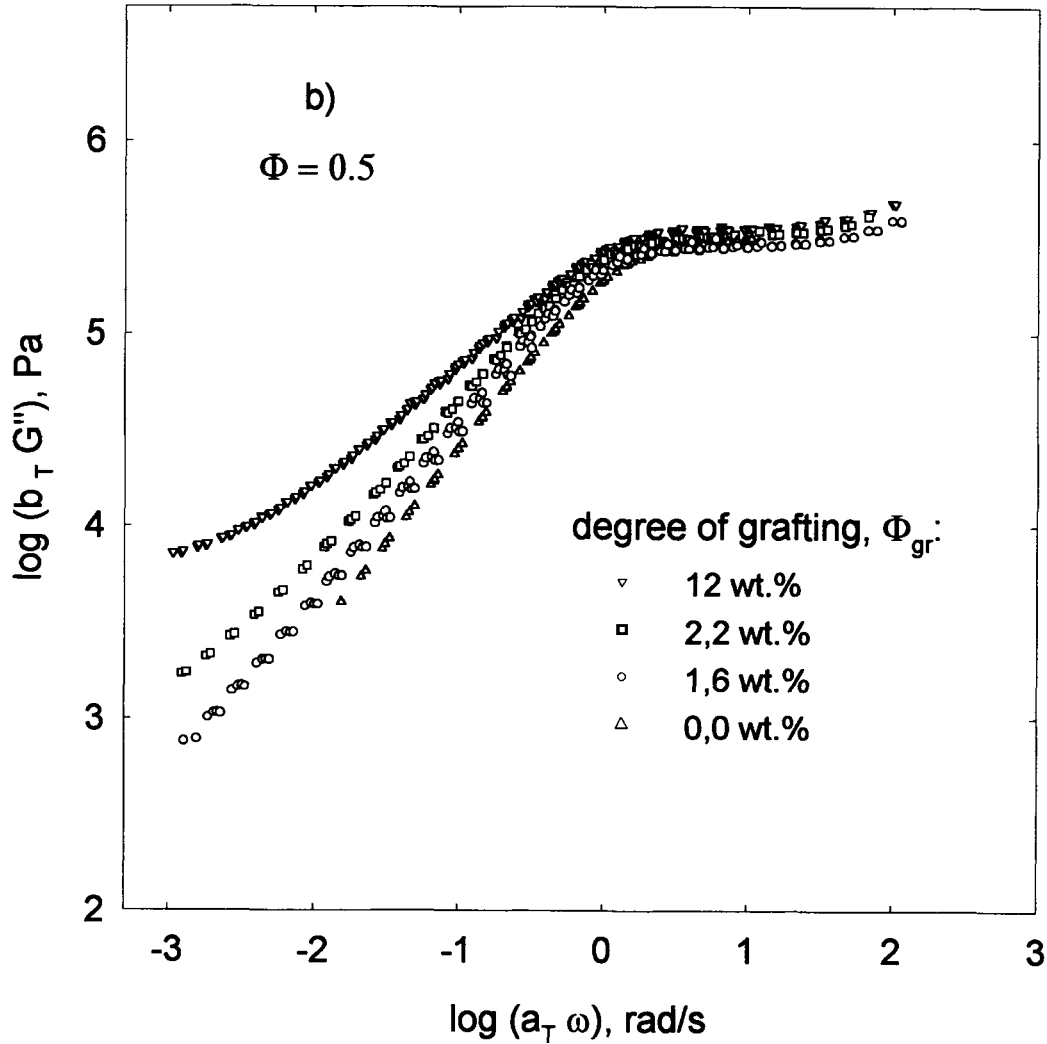


Figure 8 (continued)

the equilibrium modulus as a free parameter. The procedure is described elsewhere.<sup>11</sup>

The flow processes are unchanged under filling in so far as the observed WLF behavior is independent of the concentration  $\Phi$ . The  $C_1$  and  $C_2$  values show a relatively large scatter about the values for PS (given by the straight line in Fig. 5). Nevertheless, this behavior of a concentration-independent representation is also observed for other filled systems.<sup>10</sup>

The concentration dependence of the concentration shift follows eq. (1), which leads to a generalized Maron-Pierce equation<sup>4</sup> for the viscosity [see eq. (3)]. The parameters  $d_0$  and  $d_1$  are to be determined by the fit:

$$\log b_\Phi = \log(1 - d_1\Phi)^{d_0} \quad (1)$$

In this equation,  $d_0 = 2$ , and  $d_1^{-1} = \Phi_{\max}$  is the

maximum packing fraction. Equation (1) corresponds to the line drawn through the open squares in Figure 6. It is clear that the relative plateau modulus follows the same functional dependence. Because the Newtonian viscosity of a monodisperse material can be calculated on the basis of the following formula:

$$\eta_{0\Phi} = G_{p\Phi} \lambda_{0\Phi} \quad (2)$$

and because the terminal relaxation time,  $\lambda_{0\Phi}$ , is concentration-independent (the horizontal shift factor  $a_\Phi$  does not depend on concentration  $\Phi$ ), the following result is obtained:

$$\eta_{0\Phi} = \frac{\eta_{00}}{(1 - d_1\Phi)^{d_0}} \quad (3)$$

with  $\eta_{00} = G_{p0} \lambda_{00}$ , where  $\lambda_{00}$  is the terminal relaxation time of the matrix. Thus, the viscosity follows a percolationlike ansatz, but with a value for the maximal packing fraction  $\Phi_{\max} = 0.9$ . Considering the high polydispersity of the glass beads, this value seems to be realistic. The value  $d_1 = 1.81$  is in the range of the Maron–Pearce value ( $d_{\text{IMP}} = 2$ ). An approximation of eq. (3) for small concentrations,  $\eta_{0\Phi} \approx \eta_{00} (1 + d_0 d_1 \Phi)$ , yields the well-known Einstein formula with a coefficient ( $d_0 d_1 = 2.03$ ) relatively close to 2.5. This is surprising because concentrations up to 60% with a spacing of 10% are included in the analysis.

The thermorheological properties of composites filled with modified glass beads also follow the WLF behavior. Despite the fact that there is a large scatter in the  $C_1$  and  $C_2$  data (filled symbols in Fig. 5), the values are located around the average value of the PS matrix. The vertical shift factor is nearly the same as in the case of unmodified glass beads. It seems that the thermorheological behavior of the composites with modified glass beads is not affected by this surface modification.

In the case of the modified glass beads, the vertical shift factor for the concentration shift (filled symbols in Fig. 6) follows the same concentration dependence as in the case of the unmodified [see eq. (1)]. In contrast to the latter, an unrealistically high maximal packing fraction  $\Phi_{\max} = 1.12$  is observed. The value of  $d_1$  ( $= 3.4$ ) therefore is much higher. This may be a result of the large scatter in these data compared with those of the unmodified beads.

The Newtonian viscosity of the composites with modified glass beads cannot be determined. This leads to the following speculations: First of all, this may be a result of the (experimentally not accessible) occurrence of an equilibrium modulus at very low frequencies. In this case, the composite loses its ability to flow and shows solidlike behavior. However, the curves in Figure 7, rather, give evidence that a further relaxation process is responsible for

the data in this frequency region. We argue that this is the transition region (from lower to higher frequencies) from the slowest relaxation process, responsible for the hindered flow of the modified spheres or clusters of them, to the relaxation process characteristic for unmodified glass beads (plateau region). If this is true, the material should flow ( $G' \propto \omega^2$ ,  $G'' \propto \omega$ ) for very low frequencies or very large times. For the calculation of the Newtonian viscosity, eq. (2) is still valid. Now, we have to use a concentration-dependent (depending on the degree of filling, as well as on the degree of modification) relaxation time which is not available from our experimental data. The determination of this time should be based on creep experiments and will be a task for the future.

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