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# Elastic Properties of Polymer Melts Filled with Nanoparticles

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**Abstract.** The influence of silica nanoparticles on the elasticity of a polymethylmethacrylate (PMMA) melt was investigated. The extrudate swell obtained from the extrusion of the melt through a die and the recoverable deformation after a creep test were measured. As well known from other materials, the extrudate swell becomes smaller by adding fillers, i.e. the elasticity decreases. This is usually explained by the effect of substituting viscoelastic polymer molecules by rigid particles. The linear steady-state recoverable compliance  $J_e^0$ , however, attains values which are significantly higher than those of the matrix indicating an increase of the elasticity. This effect is postulated to be due to interactions of the matrix molecules with the particle surface giving rise to longer retardation times and higher retardation strengths which lead to larger  $J_e^0$  according to the theory of linear viscoelasticity. The apparent discrepancy between these two contrary effects is solved by the finding that the recoverable compliance becomes smaller with stress above a critical value and approaches the elasticity of the matrix. This decrease is found in a stress range which is much lower than that applied in the extrudate-swell experiment. The results of an elastic compliance becoming smaller with stress are interpreted by a detachment of the matrix molecules from the particles.

**Keywords:** Extrudate swell, Steady-state elastic compliance, Creep-recovery experiments, Polymethylmethacrylate, Silica nanoparticles, Particle/matrix interaction model.

**PACS:** 83.60.Jk, 83.85.Tz

## INTRODUCTION

The distinguished viscoelastic behavior of polymer materials which is the physical reason for their pronounced time dependence can be regarded as one of their most remarkable features. Whereas the viscosity is widely used for the characterization of polymers and an assessment of their processability, elastic effects of a melt play a comparably minor role, although they are able to very sensitively reflect some features of the molecular structure of a polymer. Furthermore, the elasticity may affect properties of manufactured items like the geometry of extruded parts or internal stresses within injection molded ones. A very obvious appearance of elasticity is the so-called extrudate swell which can be observed while extruding a melt through a die. Other phenomena reflecting the elasticity of polymers melts are the occurrence of normal stress differences during shearing and the existence of storage moduli and elastic compliances in dynamic-mechanical experiments. Recovery experiments after deformation in shear or elongation can be used to get an insight into elasticity, too.

These effects are the base of experimental devices for the determination of elasticity. Exploiting them, one has to be aware of their advantages and disadvantages. Measurements of extrudate swell and recovery in elongation are mainly performed in the nonlinear regime of deformation, dynamic-mechanical and creep experiments from which the recoverable compliance can be determined are conveniently carried out in the linear range. The normal stress difference can be obtained in the linear and the nonlinear regime but it is difficult to measure with good accuracy and, therefore, not widely used.

Some elastic properties of polystyrenes can be found in the literature, e.g. [1], those on polyethylenes in e.g. [2], and on polypropylenes in e.g. [3]. Much less is known on elastic properties of particle filled polymer melts although they play an important role in applications. One reason for this is the finding, that the extrudate swell decreases with growing filler content and becomes less and less prominent. This observation is normally explained by the rigid fillers substituting viscoelastic molecules. Very recent results of elasticity measurements on polymers filled with nanoparticles have demonstrated, however, that this widely used interpretation is not generally valid for all elastic effects of filled polymers, not even in a qualitative way [4, 5]. This paper intends to throw some light on these findings and to contribute to better understanding them.

## MATERIALS

Polymethylmethacrylate (PMMA) from Evonik, Germany, was used as the matrix material. Its mass average molar mass was  $M_w = 84\,000\text{ g}\cdot\text{mol}^{-1}$  and its polydispersity factor  $M_w/M_n = 1.6$  with  $M_n$  being the number average molar mass. As fillers,  $\text{SiO}_2$  particles from two different suppliers were taken. Their nominal average diameters were 20 and 70 nm. The smallest spheres of 20 nm in diameter could not homogeneously be dispersed, but the agglomerates had an average size smaller than 200 nm and showed a pronounced porosity.

## EXPERIMENTAL METHODS

The extrudate swell was measured using a commercial melt indexer. Instead of the standard die another one with a slightly different geometry was applied. Its length was chosen as  $L = 15.4\text{ mm}$  and its diameter as  $d_0 = 3.8\text{ mm}$ . The inner diameter of the barrel was 9.550 mm. For the determination of the extrudate swell defined as

$$A = d/d_0 - 1, \quad (1)$$

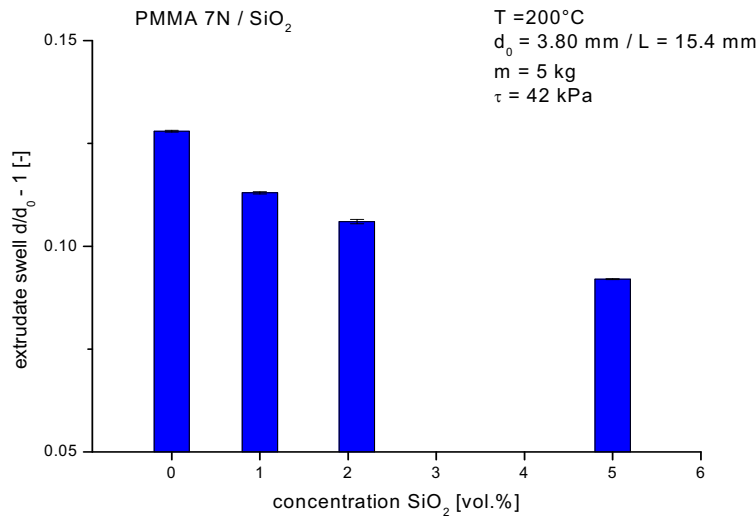
the diameter  $d$  of the extruded strand annealed to its equilibrium state was taken.

For the description of the elastic behavior in the linear regime of deformation the linear steady-state compliance  $J_e^0$  is used. This quantity can, in principle, be determined from dynamic-mechanical experiments. As this method often provides reliable data only above angular frequencies of  $\omega = 10^{-2}\text{ s}^{-1}$ , it is not well suited to

investigate molecular processes within a time frame larger than 100 s. It is well known that long molecules or pronounced branches can give rise to much longer times of molecular interactions and, therefore, dynamic-mechanical experiments may be a very limited tool if relaxation spectra over a wide range of times are required. From simple rheological experiments on particle filled polymers the occurrence of long relaxation times is obvious. Therefore, creep-recovery experiments are chosen to investigate elastic properties, the duration of which can be adapted to the time frame of the molecular processes investigated. A description of this method can be found e.g. in [6].

## RESULTS AND DISCUSSION

In Figure 1 the extrudate swell of the PMMA filled with different amounts of the nano-SiO<sub>2</sub> with a nominal particle size of 20 nm is presented. For the applied weight of 5 kg, the apparent shear stress at the wall of the die (no Bagley correction) is  $\tau = 42$  kPa. As can be seen, the extrudate swell significantly decreases with growing particle concentration although the filler content is still rather low. This result is in agreement with the text book knowledge about the influence of rigid particles on extrudate swell and, as it is frequently concluded, on the elasticity of polymer melts.



**FIGURE 1.** Extrudate swell of PMMA with silica nanoparticles.

In Figure 2 creep recovery experiments on the same kind of filled PMMA are presented. For the creep compliance  $J(t)$  and the recoverable compliance  $J_r(t_r)$  the same time scale is used. As can be seen  $J_r(t_r)$  approaches a steady state, i.e.

$$\lim_{\substack{t \rightarrow \infty \\ \tau_0 \rightarrow 0}} J_r(t) = J_e^0, \quad (2)$$

$J_e^0$  is the linear steady-state elastic compliance. For the chosen constant shear stress of  $\tau_0 = 50$  Pa it has been shown that the experiment is performed in the linear range of deformation. The linear creep compliance is given then by

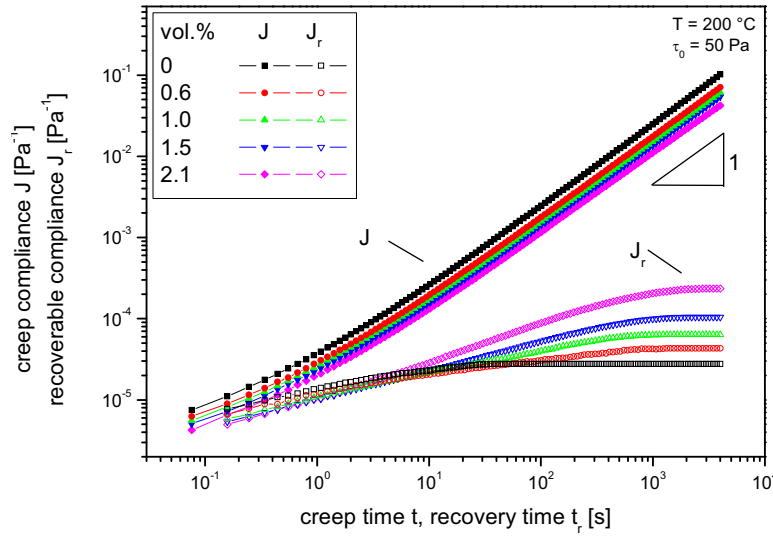
$$J(t) = J_r(t) + t / \eta_0, \quad (3)$$

$\eta_0$  being the zero shear viscosity. For  $J_e^0 \ll t/\eta_0$ , which, in principle, can always be reached at long enough creep times, Eq. 3 reads

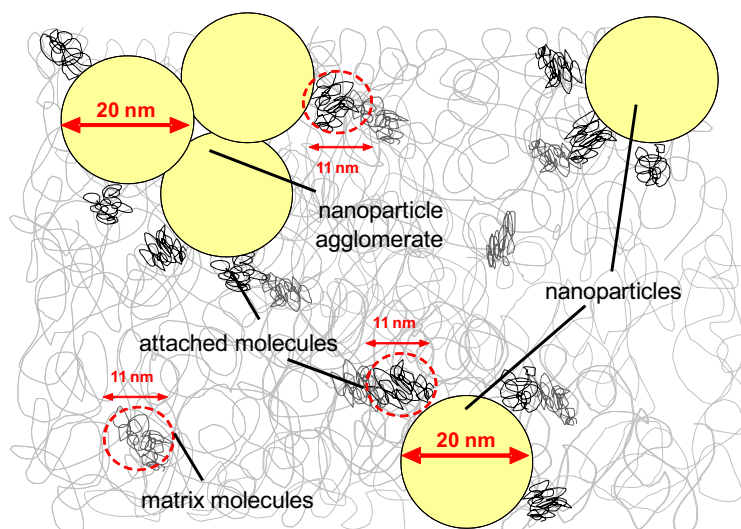
$$\lim_{t \rightarrow \infty} J(t) = t / \eta_0, \quad (4)$$

That means,  $\eta_0$  can be determined from the creep curve.

From Figure 2 it is evident that  $J_e^0$  becomes significantly larger with the addition of the nanoparticles, i.e. the elastic effect increases. This result obviously stands in contrast to the conclusions from the measurements of the extrudate swell in Figure 1 indicating a decrease of elasticity if particles are added. This apparent discrepancy is discussed in the following.

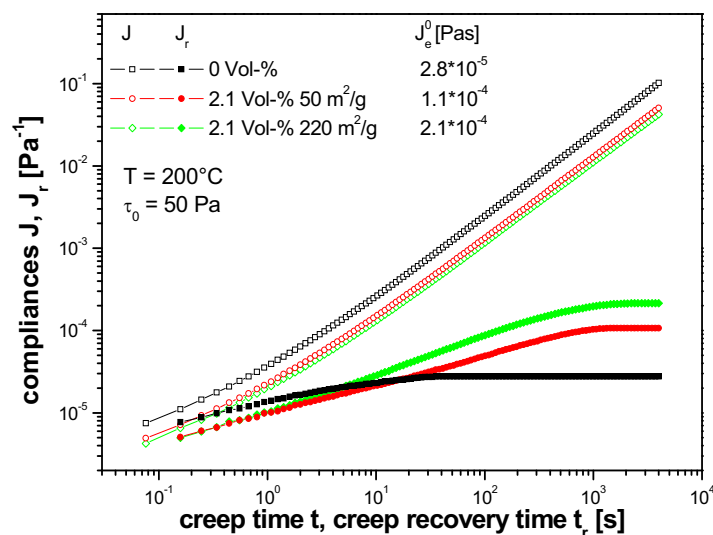


**FIGURE 2.** Creep and creep recovery curves of PMMA filled with various contents of silica nanoparticles of the nominal diameter of 20 nm.



**FIGURE 3.** Model for interactions between matrix molecules and particles.

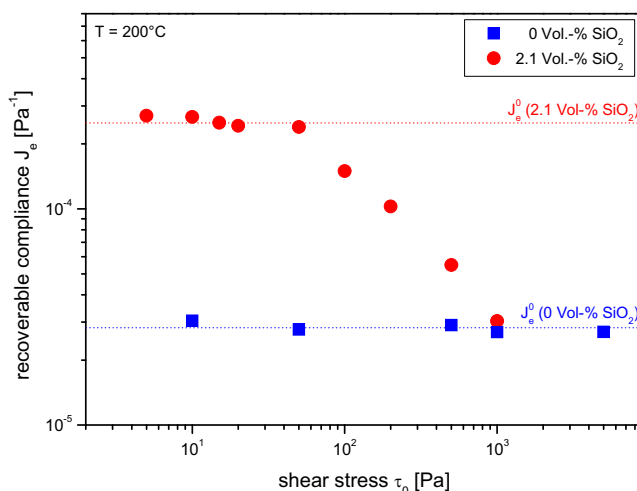
In [5] it is shown that the retardation spectra of the filled samples presented in Figure 2 are distinguished from that of the neat PMMA by pronounced maxima which become higher with increasing concentration, i.e. with growing particle surface area. This analysis leads to the model sketched in Figure 3 [5]. It visualises the idea that some of the matrix molecules may be attached to the particle surface resulting in some loss of their mobility. This effect could be the reason for higher retardation times and strengths and, following from that, to larger values of  $J_e^0$  as this quantity is the integral over the retardation spectrum according to the theory of linear viscoelasticity.



**FIGURE 4.** Creep and creep-recovery curves for PMMA with silica nanoparticles of the same concentration but different specific surface areas.

The model is supported by the results presented in Figure 4. They show the creep and creep-recovery curves of PMMA with two silica fillers of the same concentration but different specific surface areas. Whereas an influence of the specific surface area cannot be observed for  $J(t)$ , its effect is distinctly reflected by  $J_e^0$ . The enhancement of the surface area from  $50 \text{ m}^2 \cdot \text{g}^{-1}$  to  $220 \text{ m}^2 \cdot \text{g}^{-1}$  increases  $J_e^0$  by a factor of 2.

Another check for the relevance of the model is, that the elasticity should decrease and approach that one of the matrix if the molecules become detached from the particles. In order to follow up this consequence, creep-recovery experiments at higher stresses were performed. Their results are presented in Figure 5.



**FIGURE 5.** Stress dependence of the steady-state elastic compliance for the neat PMMA and PMMA filled with 2.1 vol. % of the silica with the nominal diameter of 20 nm.

Changing the applied stress between 10 Pa and 5,000 Pa does not alter  $J_e$  of the neat PMMA, i.e. the matrix material is linear in this stress range. The steady-state recoverable compliance of the filled PMMA changes significantly, however. Up to a stress of around 50 Pa it remains constant but then goes down with higher stresses reaching the value of the matrix at about 1,000 Pa. Measurements at still larger stresses were not well defined any more as fracturing of the sample at the rim of the rheometer plates occurred.

The results of a steady-state elastic compliance decreasing with stress above a certain critical value are the key for an understanding of the discrepancy that the extrudate swell reflecting the elasticity of a polymer melt decreases with filler addition but the linear steady-state elastic compliance becomes larger. As follows from the Figures 1 and 2 the stresses at which the experiments were performed differ by a factor of nearly 1000, i.e. the extrusion took place under pronounced nonlinear conditions. Stresses small enough to reach the linear regime are not possible due to the measuring principle of capillary experiments and their limitations in accuracy.

## CONCLUSIONS

There are two different effects which determine the elasticity of filled polymer melts. On the one hand, the substitution of viscoelastic polymer molecules by rigid particles generally leads to a decrease of elasticity. On the other, attachments of matrix molecules to the particle surfaces can give rise to an enhancement of the elasticity due to the reduction of their mobility which results in longer retardation times and higher retardation strengths. These mechanisms counteract each other. The increased linear steady-state elastic compliance of PMMA filled with silica nanoparticles indicates that the interaction effect exceeds that of the substitution. The well-known findings that the extrudate swell of polymer melts containing micro-sized particles decreases with growing filler concentration point to the substitution effect being superior to that of the surface interactions.

This model is too simplified, however, as the results of a decreasing extrudate swell but an increasing linear steady-state elastic compliance obtained for the PMMA filled with the same silica nanoparticles demonstrate. The matrix/particle interaction can be diminished by applying stresses to the sample which are able to detach the molecules. This effect results in a smaller elasticity. Such stresses are easily reached in the capillary experiments used for the measurements of extrudate swell. That means, only the substitution effect comes into play under these conditions.

The results presented convincingly show, that from measurements of the recoverable creep-compliance interesting conclusions regarding particle/matrix interactions can be drawn. For example, the stress at which the linear steady-state recoverable compliance starts to become smaller may give a hint to the lowest interaction forces occurring.

Furthermore, it becomes obvious from the results presented that creep-recovery measurements are a very effective method to extend the mechanical spectroscopy to time frames not available from the widely used dynamic-mechanical experiments.

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