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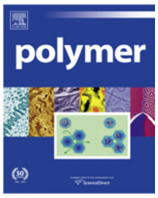

Viscous and elastic properties of poly(methyl methacrylate) melts filled with silica nanoparticles

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ABSTRACT

In this paper it is shown that elastic properties of a poly(methyl methacrylate) melt in the linear range of deformation are more significantly influenced by the addition of silica nanoparticles than viscous ones. The effect is the strongest in the steady-state which is reached at several thousand seconds. That is the reason why the often used dynamic-mechanical experiments are not a very suitable method for investigations of that kind. Therefore, creep and creep-recovery tests were applied for the characterisation of the filled materials. The linear steady-state recoverable compliances following from the recovery experiments increase by a factor of 6 at the highest measured volume content of 2.1%. This finding is explained by the existence of long retardation times in the filled materials resulting from interactions between the fillers and matrix molecules attached to their surfaces which reduce their molecular mobility. Retardation spectra calculated from the recovery curves quantify these assumptions. The model is supported by the experimental finding that the recoverable compliance becomes smaller above a certain stress applied and approaches that of the matrix as such a behaviour could be explained by a detachment of the molecules from the particle surface. The paper demonstrates that investigations of elastic properties of nanoparticle filled polymers in the molten state at long experimental times are a very sensitive tool to get an insight into interactions between particles and macromolecules of such systems.

1. Introduction

Nanoparticle filled polymers are becoming more and more interesting for applications. In most cases the particles are brought into the polymer materials in the molten state. As it is well known rheological properties of a material can change significantly by such a modification. Since they are very important for an assessment of the processing behaviour, increasing the knowledge about correlations between properties of particles and their influence on the rheology of the compounds is of great scientific actuality. Besides this processing related aspect any method which would be able to contribute to a deeper understanding of the interactions between nanoparticles and the molecules of the matrix they are filled in is of interest. Besides an enrichment of fundamental knowledge, investigations of that kind could have an impact on practical aspects like the dispersion of nanoparticles which is one of the decisive issues to be solved in order to exploit their potential with respect to an effective improvement of material properties. This indirect way of analysing the distribution of particles within a polymer matrix is of advantages if compared to the widely used transmission electron microscopy since rheological measurements integrate over the whole sample under investigation whereas microscopic imaging is always restricted to a very small part of a sample.

Dynamic-mechanical or creep-recovery experiments, in particular, are very suitable to get an insight into interactions which influence the mobility of molecules as relaxation or retardation spectra can be calculated from them. The mechanical spectroscopy can be used as a powerful tool to detect changes of the time-scales underlying molecular interactions.

With these general aspects in mind dynamical-mechanical and creep-recovery experiments were carried out on a poly(methyl methacrylate) (PMMA) filled with different concentrations of silica nanoparticles.

The literature on creep and creep-recovery experiments to investigate the time behaviour of nanoparticle filled polymers is very rare. Lim et al. [1] performed such tests on a biodegradable aliphatic polyester filled with an intercalated clay. The experimental parameters were rather undefined and, therefore, only very qualitative conclusions can be drawn from the results. Well defined creep-recovery experiments on polyisobutylene filled with silica particles in the range of several micrometers were carried out by

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Schmidt and Münstedt [2]. They found a remarkably large elasticity at low shear stresses which nearly disappeared at higher ones. Because of the relatively big particles and the high filler content these systems are not directly comparable to those discussed in this paper, however.

Dynamic-mechanical experiments are more often used to characterise nanoparticle filled polymers. In nearly all cases their aim is to get some insight into the formation of a network by the particles added, which is indicated by the storage modulus G′ becoming more and more independent of frequency. For example, Cassagnau [3] investigated the frequency dependence of polystyrene/SiO_2 nanocomposites and found a plateau at low frequencies around 5 vol.%. Conclusions with respect to the rheological behaviour at lower frequencies were not drawn. In a paper by Garcia et al. [4] the network formation in polyamide 6 with SiO_2-nanoparticles is discussed and Tan et al. [5], for example, investigated the dynamic-mechanical behaviour of SiO_2-particles in an ethylene-propylene-diene-rubber.

From this survey it becomes obvious that the topic of this paper covers an area hardly discussed in literature, namely the rheological analysis of sparsely filled polymer/nanoparticle compounds at long time-scales.

2. Experimental

As the matrix material PMMA 7N of the Evonik company was used. It was filled with silica nanoparticles from ChemPur GmbH the nominal particle size of which was 20 nm. The compounds were prepared in solution. Dichloroethane was found to be most suitable but even with this solvent the complete separation of the silica agglomerates into the primary particles was not possible as Fig. 1a demonstrates. Besides rather small particles of the size of several 10 nm, aggregates with diameters of around two hundred nanometers can be seen in the TEM micrographs. As becomes evident from Fig. 1b these aggregates possess significant porous structures which give rise to much larger surface areas than calculated from their outer geometrical dimensions. These features mean that the specific surface area available for interactions between fillers and matrix molecules is smaller than that in case of the totally dispersed 20 nm particles but remarkably larger than that of agglomerates with a nonporous structure.

For the rheological measurements a Bohlin CSM 50 of Malvern Instruments was used. The dynamic-mechanical and the creep and creep-recovery experiments as well were performed with pressed samples of 25 mm in diameter and 2 mm in height. The Bohlin CSM rheometer is particularly suitable for creep experiments as it is stress controlled. The performance of dynamic-mechanical experiments and their evaluation are state of the art. General information about the less common creep and creep-recovery tests can be found, for example, in Schwarzl [6] and a detailed instruction how to perform them successfully in Gabriel and Kaschta [7].

3. Results and discussion

3.1. Thermal stability

A precondition for reliable rheological experiments particularly at longer measuring times and higher temperatures is the thermal stability of the material. A very sensitive method to get an insight into this behaviour are measurements of the storage modulus G′ as a function of time at a definite temperature. The frequency should be chosen as low as possible since a change of the molar mass is reflected most distinctly in the terminal range. On the other hand, over the duration of the experiment a reasonable number of measuring points should be available to give reliable pictures. Fig. 2

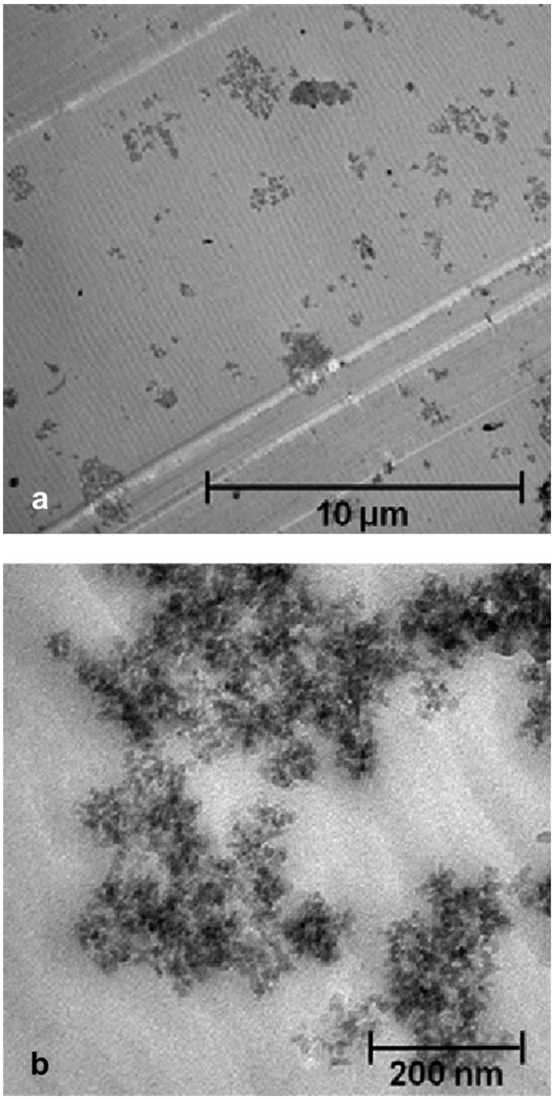

Fig. 1. Dispersion of 2.1 vol.% nanosilica particles in PMMA 7N (a) and the typical feature of agglomerates (b).

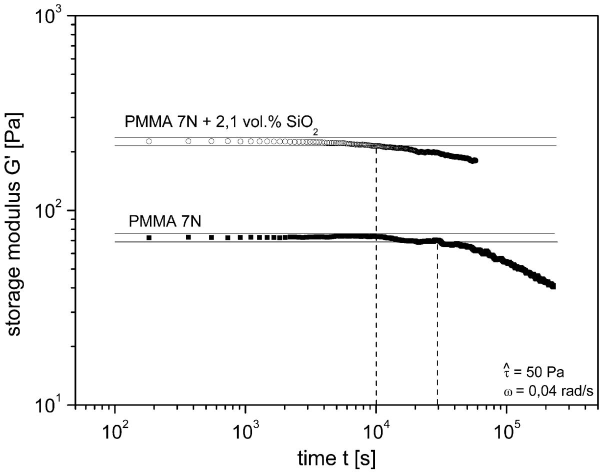

Fig. 2. Stability tests of PMMA 7N without and with fillers at 200 °C.

presents $G'(t)$ at $\omega = 0.04\ \mathrm{s}^{-1}$ for the neat PMMA and the PMMA filled with 2.1 vol.% silica nanoparticles the highest concentration applied for creep and creep-recovery experiments. A material is defined to be thermally stable if it does not deviate more than 5% from the initial value. The longest time over which this condition is fulfilled is denominated the stability time t_{stab}. As can be seen from Fig. 2 t_{stab} is 30,000 s for the neat PMMA and it decreases to around 10,000 s for PMMA with 2.1 vol.% fillers at a temperature of 200 °C. Despite these limitations the stability of the materials is high enough for performing creep and creep- recovery experiments.

3.2. Dynamic-mechanical experiments

In Fig. 3 the storage modulus G' is plotted as a function of the angular frequency ω for PMMA filled with different concentrations of the nanosilica. The results demonstrate that G' very sensitively reacts on the filler content. The modulus increases with the amount of fillers and reaches an approximately frequency-independent plateau at the highest concentration of 10 vol.%. Such a behaviour indicates the formation of a network by the particles. A network structure which can sensitively be investigated by dynamic-mechanical experiments is not the content of this paper, however. Its topic is rather related to the interactions between particles and matrix molecules. They can be investigated at lower concentrations at which a particle network does not exist. At a concentration of only 0.6 vol.% a clear deviation of $G'(\omega)$ from the curve of the unfilled PMMA is already visible. Increasing the concentration up to 2.1 vol.% results in a further but relatively small growth of G′ at the lowest frequency of $0.04\ \mathrm{s}^{-1}$. As the terminal regime is not reached, from experiments at smaller frequencies a clearer distinction of the influence of the particles could be expected. Dynamic-mechanical experiments do show principal limitations, however, to investigate processes with very long relaxation times as each frequency change starts a new cycle which has to reach its steady-state in order to deliver time-independent data from which conclusions with respect to molecular processes can be drawn. According to Schwarzl [6] it takes six cycles to achieve a relative uncertainty smaller than 1%. For an angular frequency of $10^{-3}\ \mathrm{s}^{-1}$ this would mean an experimental time of 6000 s and for $10^{-4}\ \mathrm{s}^{-1}$ even 60,000 s. Due to the extremely long times necessary for a comprehensive dynamic-mechanical experiment the thermal stability of polymer samples normally will not be high enough to obtain reliable data.

3.3. Creep-recovery experiments

An elegant method to get insight into long relaxation or retardation times, respectively, are creep and creep-recovery experiments. Measurements of that kind on the filled PMMA samples are presented in Fig. 4. The upper curves represent the creep compliances J_{cr} defined as

$$J_{\mathrm{cr}}(t_{\mathrm{cr}}) = \frac{\gamma(t_{\mathrm{cr}})}{\tau_0} = J_0 + \psi(t_{\mathrm{cr}}) + \frac{t_{\mathrm{cr}}}{\eta} \tag{1}$$

as a function of the creep time t_{cr}. J_0 is the spontaneous elastic compliance, ψ the so-called creep function and η the shear viscosity which becomes η_0 in the linear range. ψ is defined as

$$\psi = \sum_{\mathrm{i}} J_{\mathrm{i}}\left(1 - \exp\left(\frac{-t}{\tau_{\mathrm{i}}}\right)\right) \tag{2}$$

with the retardation strengths J_{i} and the retardation times τ_{i}.

For the recoverable compliance J_{r} it follows

$$J_{\mathrm{r}}(t_{\mathrm{r}}) = J_0 + \psi(t_{\mathrm{r}}) = J_0 + \sum_{\mathrm{i}} J_{\mathrm{i}}\left(1 - \exp\left(\frac{-t_{\mathrm{r}}}{\tau_{\mathrm{i}}}\right)\right) \tag{3}$$

and as J_0 for polymer melts is negligibly small compared to ψ

$$J_{\mathrm{r}}(t_{\mathrm{r}}) = \sum_{\mathrm{i}} J_{\mathrm{i}}\left(1 - \exp\left(\frac{-t_{\mathrm{r}}}{\tau_{\mathrm{i}}}\right)\right) \tag{4}$$

For very long creep times t_{cr}, Eq. (1) can be written as

$$J_{\mathrm{cr}} = \frac{t_{\mathrm{cr}}}{\eta} \quad \text{or} \quad \lg J_{\mathrm{cr}} = \lg t_{\mathrm{cr}} - \lg \eta \tag{5}$$

For all the creep curves in Fig. 4 a linear range with the slope 1 in the double logarithmic plot is reached within the chosen time window of 4000 s indicating that the compliance follows in good approximation Eq. (5). From the intercept the viscosity can be calculated. It obviously increases with the filler content.

The lower curves of Fig. 4 represent the recoverable compliance J_{r}. As the experiments were performed in the linear range of deformation, in good approximation this quantity reaches the linear steady-state recoverable compliance J_e^0 within the chosen recovery time of 4000 s. J_e^0 is attained at the smaller times the lower the concentration. The filler effect on J_e^0 is found to be very pronounced. This quantity increases by a factor of about ten by

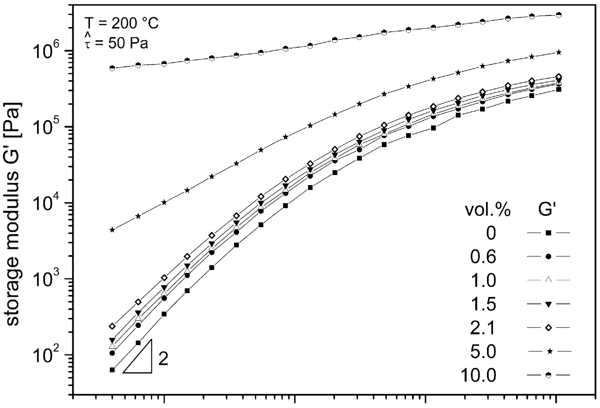

Fig. 3. Storage modulus as a function of angular frequency for PMMA 7N filled with various volume concentrations of SiO_2.

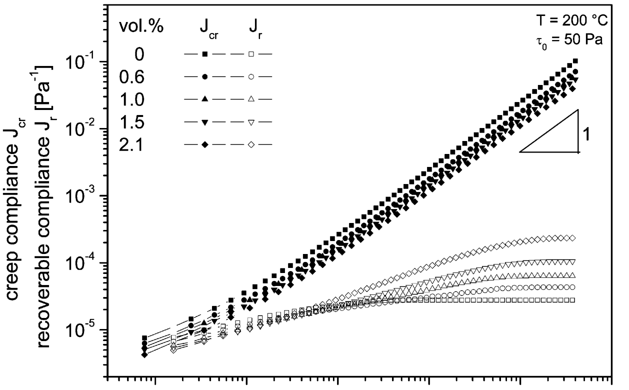

Fig. 4. Creep and creep-recovery experiments on PMMA 7N filled with various volume concentrations of SiO_2-nanoparticles.

adding 2.1 vol.%, only, and, therefore, very sensitively reacts on the filler content.

An interesting comparison of the steady-state viscosities obtained from dynamic-mechanical and creep experiments is presented in Fig. 5. The quantity t_{cr}/J_{cr} which according to Eq. (5) approaches the viscosity at long enough times is plotted as a function of the creep time. A plateau value is attained for all the samples. As expected, the time at which it is reached is the longer the higher the concentration. This result clearly demonstrates that for the chosen creep time of 4000 s the steady-state in creep is attained which is one precondition for the determination of the steady-state recoverable compliance in the following recovery experiment.

The comparison with the magnitude of the complex viscosity plotted as a function of the angular frequency ω demonstrates that smaller ω would be necessary to convincingly reach the steady-state. The interesting feature, however, is that the steady-state values according to the two experimental modes seem to be very close to each other demonstrating the accuracy and compatibility of the two different experimental methods.

In Fig. 6 η_0 and J_e^0 are presented as functions of the filler content. Whereas a weak linear increase of the viscosity with filler concentration is found the growth of J_e^0 is distinctly stronger than linear and follows a power law. This result demonstrates that J_e^0 is a much more sensitive quantity to investigate filler/matrix interactions than the viscosity.

3.4. Retardation spectra

To get a deeper insight into molecular processes underlying the time dependence of mechanical properties the calculation of retardation and relaxation spectra can be a very useful method. The recoverable compliance in the linear range of deformation can formally be described by Eq. (4). Kaschta and Schwarzl [8] and [9] developed an algorithm to determine the retardation strengths as a function of the retardation times from creep-recovery measurements. The spectra of the samples investigated which are obtained by this method are presented in Fig. 7. The unfilled PMMA shows a small maximum, only. For the filled samples significant second maxima at longer retardation times occur which have to be related to retardation processes caused by the particles. As the concentration of the particles is so low that the distances between them are too large for any particle/particle interaction (cf. Fig. 8) some kind of interaction between the matrix molecules and the particles has to be postulated.

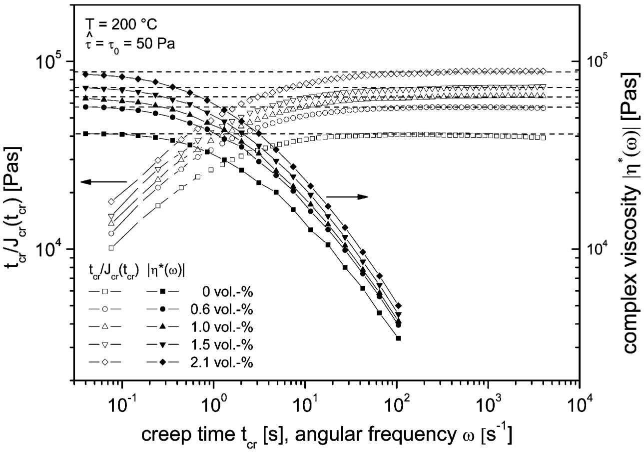

Fig. 5. $|\eta^*|$ as a function of ω in comparison with $t_{cr}/J_{cr}(t_{cr})$ in dependence on t_{cr}.

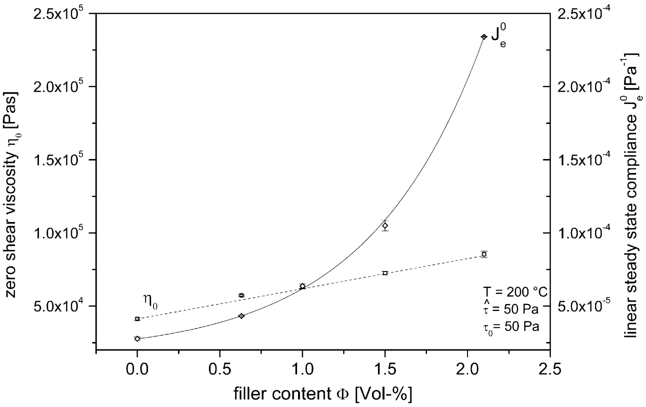

Fig. 6. Zero shear viscosity η_0 and linear steady-state elastic compliance as functions of the filler content.

3.5. Model considerations

As sketched in Fig. 8 it is assumed that some of the matrix molecules are attached to the surface of the particles by physical interactions. Such a process hinders their mobility leading to longer retardation times which are reflected by the spectrum. The height of the curves increasing with the particle concentration can be related to the higher number of particles and following from that the larger surface area available for the attachment of particles. For the observable slight shifts of the retardation times at the maxima with concentration an obvious explanation is not easy to find as the strength of interaction between the matrix molecules and the surface of the particles should not be dependent on their number as long as the distances between the particles are large in comparison to the diameters of the molecules.

The size of the molecules in relation to the particle distances can be assessed by simple considerations. The expectancy value of the squared radius of gyration of amorphous molecules follows from the well-known relationship

$$\left\langle s^2 \right\rangle = \beta^2 \cdot P \tag{6}$$

with $\beta = 0.256$ nm for PMMA according to Schwarzl [6] and $P = 510$ is the degree of polymerisation of the PMMA 7N with a number average molar mass of $M_n = 52{,}000$ g/mol. From these quantities a radius of gyration of around 5.5 nm follows.

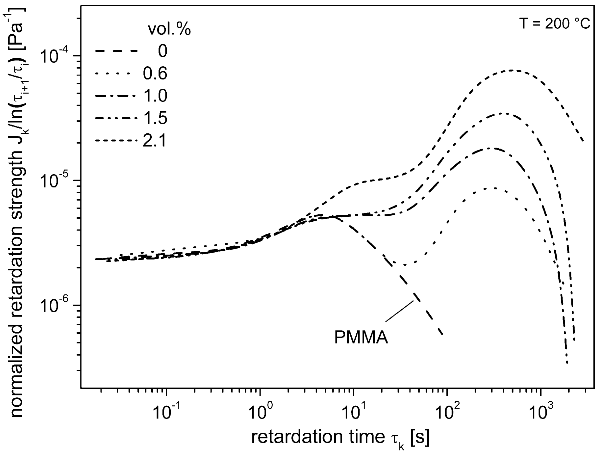

Fig. 7. Retardation spectra of PMMA 7N with various concentrations of SiO_2-nanoparticles.

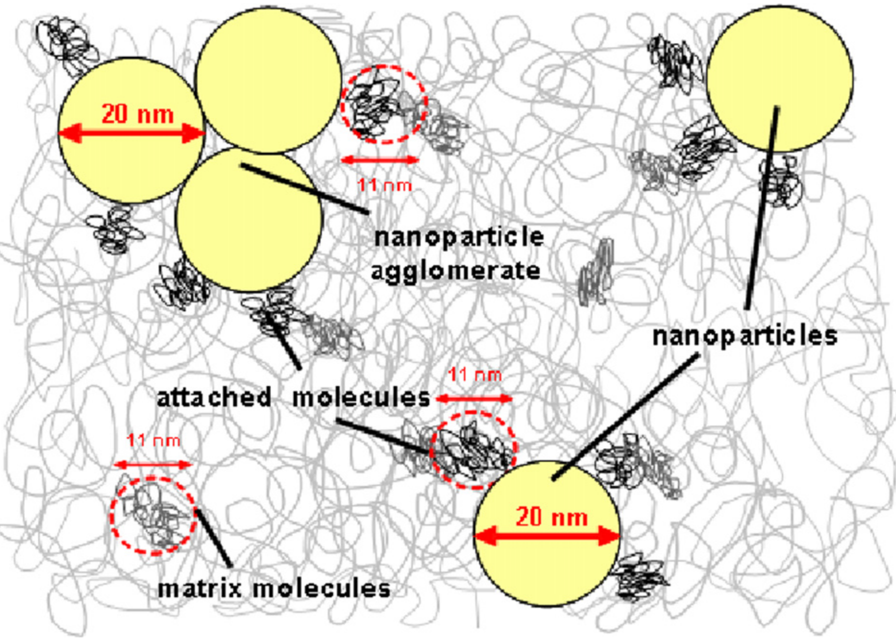

Fig. 8. Model of interactions between SiO_2-nanoparticles and polymer molecules.

The mean distance D between particles statistically distributed can be calculated according to

$$D = \left(\sqrt[3]{\frac{4\pi}{3\Phi}} - 2\right) \cdot d \tag{7}$$

Φ is the volume concentration and d the particle diameter.

In case of a volume concentration of 2.1 vol.%, fillers of 20 nm in diameter would be 38 nm apart from each other, for 50 nm this quantity is 96 nm, and for 200 nm particles 380 nm. These geometrical quantities are the base of the model picture presented in Fig. 8 for a concentration of 2.1 vol.%. It clearly demonstrates that on the average an interaction between the particles via attached molecules is not very probable and, therefore, the rheological results obtained are related to particle/molecule interactions, only.

3.6. *Stress dependence of the recoverable compliance*

If the assumption is realistic, that matrix molecules adhering to the surface of the nanoparticles are the reason for the long retardation times which determine the recoverable compliance, a change of the interaction should be reflected by the compliance. Thus, one could imagine that the number of adherent molecules and following from that the recoverable compliance are dependent on the applied stress. In Fig. 9 the results of such experiments are presented. Creep and creep-recovery measurements for the PMMA with 2.1 vol.% fillers were performed at stresses ranging from 10 Pa to 3000 Pa. The creep compliances do not show any noticeable dependence on the stress, i.e. the experiments are performed in the linear range of deformation. A totally different picture is found for the recoverable compliance. Up to applied stresses of 50 Pa the curves cannot be distinguished from each other. Starting at a stress of 100 Pa, the steady-state recoverable compliances decrease as a function of stress. The results are summarised in Fig. 10. For the matrix, constant J_e^0 are found for all the stresses applied, i.e. the PMMA shows a linear behaviour in the stress range applied. The steady-state elastic compliances of the filled samples decrease from a plateau at smaller stresses and approach the value of the matrix, i.e. a pronounced nonlinearity occurs for stresses larger than 50 Pa[1]. This effect may be due to a disintegration of attached molecules from the particle surfaces. From this result it may be concluded that the adhesion forces are high enough to withstand an applied stress of 50 Pa.

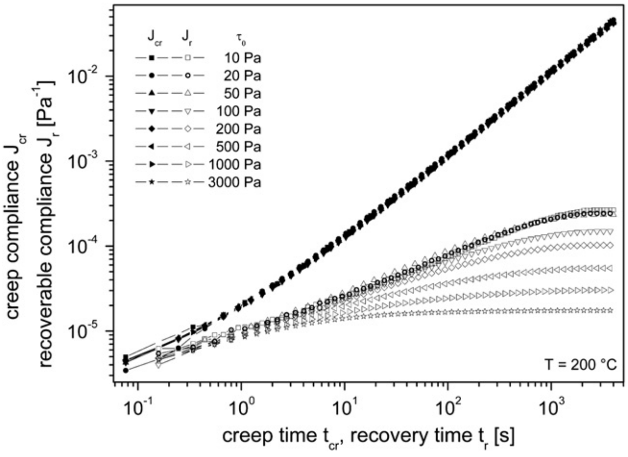

Fig. 9. Stress dependence of the creep compliance and the recoverable compliance for PMMA 7N filled with 2.1 vol.% SiO_2-nanoparticles.

An interesting feature of the recovery of the nanoparticle filled sample is documented in Fig. 11. It shows that the effect of the decrease of J_r with stress is reversible. If the sample deformed under a stress of 1000 Pa and retarded subsequently is sheared under a stress of 50 Pa again the curve of J_r comes to lie on that of the measurement without the previous test at 1000 Pa. This result implies that the detachment process is reversible. Again the creep compliance does not show any change under the conditions applied.

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[1] Measurements at stresses higher than 1000 Pa have to be regarded with caution as instabilities at the rim of the sample were observed. Therefore, the corresponding data points are marked by brackets.

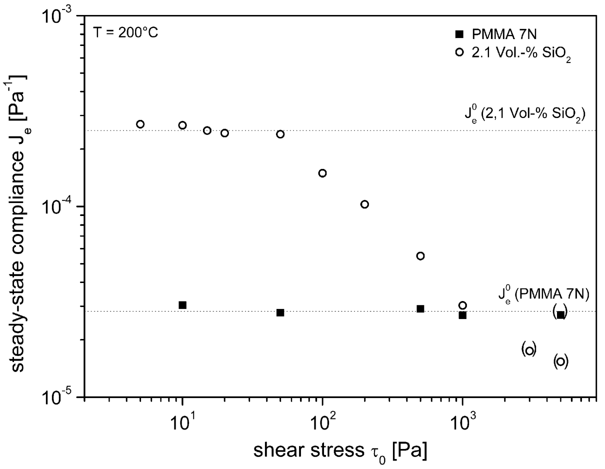

Fig. 10. Steady-state compliance as a function of the applied stress τ_0 for the unfilled and filled PMMA.

3.7. Relationship between creep-recovery and dynamic-mechanical experiments

Knowing the retardation spectrum from Eq. (4), and η_0 from the creep curves in Fig. 4 the real part J' and the imaginary part J'' of the complex compliance can be calculated according to the linear theory of viscoelasticity

$$J' = \sum_{\mathrm{i}} J_{\mathrm{i}} \frac{1}{1+\omega^2 \cdot \tau_{\mathrm{i}}^2} \tag{8}$$

and

$$J'' = \sum_{\mathrm{i}} J_{\mathrm{i}} \frac{\omega \cdot \tau_{\mathrm{i}}}{1+\omega^2 \cdot \tau_{\mathrm{i}}^2} + \frac{1}{\omega \cdot \eta_0} \tag{9}$$

The storage modulus G' and the loss modulus G'' follow from J' and J'' according to

$$G' = \frac{J'}{J'^2 + J''^2} \tag{10}$$

and

$$G'' = \frac{J''}{J'^2 + J''^2} \tag{11}$$

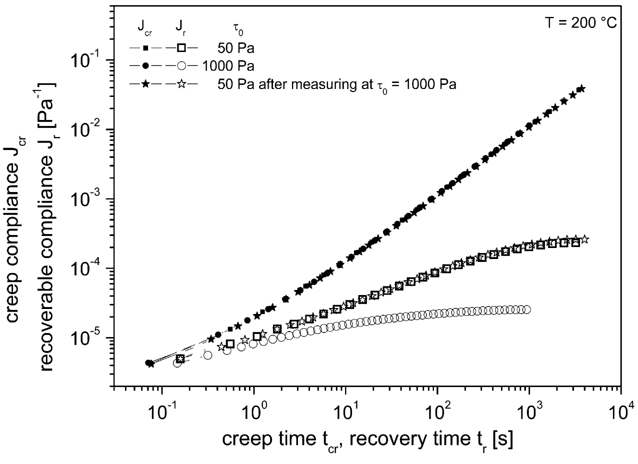

Fig. 11. Creep compliance and recoverable compliance at a high and low shear stress.

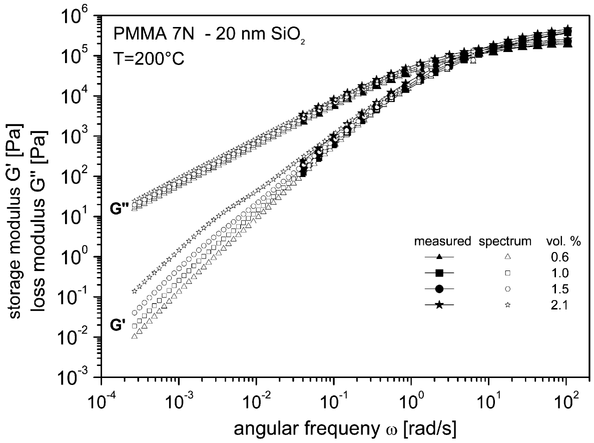

Fig. 12. Storage modulus and loss modulus for various volume concentrations of SiO_2-nanoparticles from dynamic-mechanical experiments (filled symbols) and from calculations by the retardation spectra (open symbols).

In Fig. 12 the calculated values of G' and G'' are compared with the measured ones for the four samples with different filler contents. The agreement in the overlapping regions is convincing demonstrating the compatibility of the two different modes. Moreover, applying the relationships above, $G'(\omega)$ and $G''(\omega)$ can be extended to lower frequencies which are difficult to measure. In principle, from these data relaxation spectra could be calculated using the methods known from the literature (Baumgaertel and Winter [10]). Particularly, from $G'(\omega)$ it is clearly seen that around $\omega = 10^{-2}\,\mathrm{s}^{-1}$ a second relaxation process comes into play. It is related to the filler/particle interaction and is the more pronounced the higher the particle concentration.

4. Conclusions

It has been shown that mechanical spectroscopy is a suitable method to detect slow molecular processes induced by the interaction between matrix molecules and particles if applied at low frequencies or long times, respectively. As dynamic-mechanical experiments can effectively be conducted down to angular frequencies of $10^{-2}\,\mathrm{s}^{-1}$, only, the time scale of processes to be detected is limited to 100 s. Using creep-recovery experiments a time scale of several thousand seconds can easily be covered which makes the investigation of slow processes possible. By this method it is demonstrated that in PMMA filled with nanosilica retardation processes take place at long times which give rise to a significant increase of the linear steady-state elastic compliance J_e^0. This quantity is very sensitively influenced by the surface area available for interactions and the number of molecules attached to it. This model follows from the experimental results that J_e^0 increases with the volume concentration of the filler but decreases if stresses above a certain limit are applied. The critical value can be interpreted as a quantity characterising the interaction between the PMMA molecules and the particles.

Surprising at a first glance is the finding that the viscosity which is obtained from the steady-state of the creep experiment is much less influenced by the filler particles than the elastic compliance. This observation can be taken as an indirect proof that there is no long-range interaction between the particles but that the flow behaviour can be regarded as that of a polymer matrix filled with non-interacting particles. For such systems it is well known that the viscosity increases with the filler content. Due to the low volume concentration used this effect is small, however. The model postulating interactions between polymer molecules and particles is not in contrast to that conclusion as the interaction is limited to a thin layer of one to two molecules which may increase the effective size of the filler slightly.

Calculating retardation spectra from the recovery curves is a very useful method to quantify the experiments even if a model is not available which allows a quantitative interpretation on a molecular level. Although rather formal, the spectrum is a finger print which facilitates the discussion.

Due to the sensitive influence of the specific surface area on the steady-state elastic compliance this quantity offers some potential with respect to an assessment of the quality of dispersion. The smaller the number of agglomerates at a given particle concentration the larger is the surface area available for interactions with the matrix molecules and consequently the compliance. The relevance of these relations for practical purposes has been shown in Triebel et al. [11].

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