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Rheological Properties of Poly(methyl methacrylate)/Nanoclay Composites As Investigated by Creep Recovery in Shear

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ABSTRACT: Poly(methyl methacrylate) (PMMA)/nanoclay composites with different filler fractions were prepared by a combined solution and melt mixing route. Three PMMA matrices of different molar masses but very similar polydispersities were used. Creep and creep-recovery experiments were performed in the linear and nonlinear regime. While the creep compliances remained nearly unchanged by the filler addition, the recoverable creep compliances were strongly influenced by the addition of the nanoclay in dependence on the volume fraction. Up to a 10-fold increase of the recoverable creep compliance compared to the matrix was found. The findings can be explained by assuming an interaction between some of the PMMA molecules and the particle surfaces resulting in a decline of molecular mobility.

Introduction

Polymer nanocomposites have gained growing scientific and practical interest during the past decade due to their unique properties. Fillers on a nanoscale can influence material properties more efficiently compared to microparticles of the same volume filler fraction. Mechanical, magnetic, or electrical properties can be improved while optical properties like the transparency of a matrix are sometimes only little deteriorated. For industrial applications of nanoclay composites the reduction of gas permeability and the improved flame retardance of the materials are important.[1−5]

The influence of microparticles on rheological properties of polymers has frequently been discussed in the literature.[6−8] The viscosity increase with growing filler content is well understood. However, much less has been done to get an insight into the elastic properties of dispersions. Schmidt and Münstedt[9] found from creep-recovery measurements in shear on a model suspension of SiO_2 microspheres in a Newtonian liquid that the filled systems behave Newtonian if large shear stresses are applied. In contrast, a non-Newtonian behavior arises for low shear stresses. In this case, a large elasticity was found, which was explained by a particle network existent in the suspensions under low stresses.

For different polymer systems filled with nanoclays a strong influence of the filler on rheological properties of the composites in the molten state was reported from experiments performed in oscillatory shear.[10−15] An increase of both the loss and the storage moduli was found by adding fillers. This finding was explained by the assumption of interactions of the matrix polymer with the clay which lead to longer relaxation times of those molecules interacting with the nanoparticles.

Longer relaxation times should clearly become apparent in creep-recovery tests, as they can easily be extended to the then necessary long durations of the experiments. Additional modes of longer relaxation times in the spectrum are expected to increase the recoverable compliance. However, little is known about the creep and creep-recovery behavior of nanoparticle-filled polymers. Lim et al.[12] found for an increasing filler content of intercalated clay in a biodegradable aliphatic polyester a decrease of the creep compliance and a strong increase of the recoverable compliance.

In this work, the influence of nanoclay on the viscous and elastic properties of three PMMA with various molar masses but the same polydispersity index M_w/M_n were investigated.

Experimental Section

Materials. The three PMMA used as matrix materials were Plexiglas 7N (PMMA 7N), Plexiglas 7 M (PMMA 7M), and Plexiglas 7H (PMMA 7H) from Evonik Röhm GmbH (Germany). Some of their properties are summarized in Table 1. The absolute molar masses were determined by size exclusion chromatography (SEC) with a multiangle laser light scattering (MALLS) device (miniDawn, Wyatt Technologies). The measurements were carried out at room temperature using tetrahydrofuran as solvent.

Figure 1 shows the molar mass distribution as measured by SEC-MALLS. The distributions are similar but are shifted toward higher molar masses with increasing weight-average molar mass M_w (see Table 1). The fits of a logarithmic normal distribution function to the data points are also included in Figure 1. The data are well described by the log-normal distribution function except for the low molar mass tail found for all the three samples.

M_w increases from 7N to 7H by a factor of nearly 2, whereas the polydispersity of the three products is the same within the accuracy of the measurements. The densities ρ and the glass transition temperatures T_g were found to be the same. They follow as $\rho = 1.19$ g/cm^3 and $T_g = 110$ °C.

Nanofil15 (nanoclay) supplied by Süd-Chemie (Germany) was chosen as the filler material. In order to ease its intercalation by the polymer molecules, or even achieve an exfoliation of the silicate layers, the primary cations of this clay were exchanged by dioctadecyldimethylammonium chloride. The density of the nanoclay was measured with a gas pycnometer to be 1.63 g/cm^3.

Composite Preparation. The composites were prepared in a two-step procedure. First, 15 wt % of the polymer was dissolved in chloroform. Then the clay was mixed into this solution to receive a masterbatch with 30 wt % clay after evaporation of the solvent. For a good dispersion of the particles the solution was stirred with an Ultraturrax high-speed stirrer after adding the clay. This was repeated three times whereby 1 min of agitation was followed by 1 min of rest: Afterward, the dispersion was treated in an ultrasonic bath for 30 min and then stirred for an additional 8 h.

In the second step the dried masterbatch was melt-mixed with neat polymer in a kneader at 185 °C for 10 min at 25 rpm in order to prepare the volume concentrations desired. The reference samples of the neat materials investigated were also processed, dried, and kneaded in the same way as the filled samples.

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Table 1. Material Data of the Polymers Used

	PMMA		
	7N	7M	7H
weight-average molar mass M_w [kg/mol]	84	105	141
polydispersity factor M_w/M_n	1.6	1.6	1.6
zero shear-rate viscosity η_0 at 183 °C [Pa·s]	230 000	480 000	1 500 000
steady-state recoverable compliance J_e^0 at 183 °C [10^{-5} Pa^{-1}]	2.8 ± 0.2	2.6 ± 0.2	2.9 ± 0.2

For PMMA 7N composites containing 1.7, 2.1, and 2.5 vol % of nanoclay were prepared. With the latter concentration composites using PMMA 7 M and PMMA 7H as matrices were made, too.

Sample Preparation. For rheological tests, the materials were compression-molded (185 °C, vacuum) into cylindrical plates with a diameter of 25 mm and 2 mm thickness. Prior to the blending and to the measurements the polymers and nanocomposites were dried in a vacuum oven for at least 12 h at 80 °C.

Experimental Methods. X-ray diffraction (XRD) was applied to measure the gallery spacing of the filler and to judge the degree of exfoliation. An X'pert Pro MPD from Philips using Cu Kα radiation with an acceleration voltage of 40 kV was used. The layer distance was calculated by Bragg's law from the 001 reflex. The quality of dispersion of the particles in the matrix was studied by means of transmission electron microscopy (TEM) using a JEM 200 CX (JEOL) at the National Academy of Science in Prague.

The rheological investigations were performed at $T = 183$ °C (if not indicated differently) under a nitrogen atmosphere by stress-controlled rheometers (CSM 50 and Gemini, Malvern Instruments) using a plate−plate geometry (25 mm diameter, 2 mm gap). For each run, a new sample was used. After loading the rheometer a waiting time of 7 min was applied for each test, in order to evenly adjust for the correct temperature of the sample.

Creep and creep-recovery experiments according to Figure 2 were performed. In the creep test a constant shear stress τ_0 is applied, and the resulting time-dependent deformation $\gamma(t_{cr})$ is measured. The creep compliance $J(t_{cr})$ in the linear viscoelastic range can be described by

$$J(t_{cr}) = \frac{\gamma(t_{cr})}{\tau_0} = J_0 + \Psi(t_{cr}) + t_{cr}/\eta_0 \qquad (1)$$

with J_0 being the elastic compliance, $\Psi(t_{cr})$ the viscoelastic portion of the compliance, and η_0 the zero shear-rate viscosity. In the following creep-recovery experiment the shear stress τ_0 is set to zero at t_0, and the recoverable deformation $\gamma_r(t_0, t_r)$ is measured. For a given preceding shear stress this quantity generally depends on the creep time t_0 and the recovery time t_r.

The recoverable compliance $J_r(t_0, t_r)$ as defined by

$$J_r(t_0, t_r) = \frac{\gamma_r(t_0, t_r)}{\tau_0} \quad \text{with} \quad \gamma_r(t_0, t_r) = \gamma(t_0) - \gamma(t_0, t_r) \qquad (2)$$

in the linear range of deformation is a measure of the elasticity of the material.

As the values for $J_r(t_0, t_r)$ are small compared to $J(t_{cr})$ for most polymers, a double-logarithmic plot is used in the following to present the results of the creep-recovery tests. Furthermore, for the creep and creep-recovery measurements the same time axis is used, i.e., t_r and t_{cr} as well start at the time zero (see Figures 6−12).

In all experiments the recovery times t_r were taken long enough to reach a stationary value for $\gamma_r(t_0, t_r)$. The resulting compliance is called the (stationary) recoverable compliance $J_{r,s}(t_0)$. In the linear range and for $t_0 \rightarrow \infty$ this quantity is designated as the steady-state linear recoverable compliance J_e^0. All measurements reported were performed in the linear range of deformation.

Results

Morphology. In Figure 3 the morphology of the composite materials is visualized by means of transmission electron microscopy (TEM). Because of the fact that the clay is less transparent for the electron beam than the matrix material, the filler appears in black or dark gray.

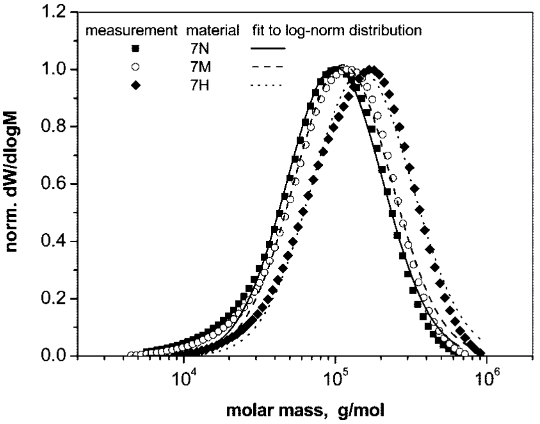

Figure 1. Molar mass distributions of the PMMA grades under investigation and the fits to a log-normal molar mass distribution.

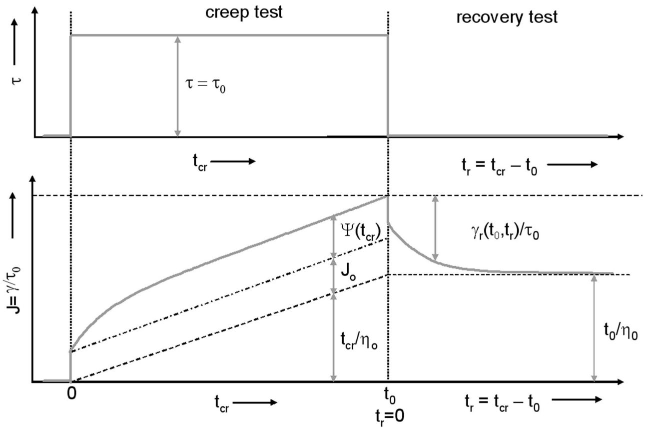

Figure 2. Schematic diagram of a creep-recovery test.

It is obvious that for all the three PMMA matrices of different weight-average molar masses the filler is evenly dispersed in the matrix without forming large agglomerates. The images in Figure 3 show cuts in arbitrary directions to the axis of the filler particles. Therefore, the surface area of the platelets becomes visible as well as the thickness of single layers or staples of layers. At a first glance the particles in Figure 3a show a slight orientation. However, pictures with different magnification reveal that this is just accidental. In general, the filler platelets are not oriented as can be seen in Figure 3c,d. At the higher magnification of Figure 3b single exfoliated plates as well as stacks of several platelets can be identified. However, a complete exfoliation of the clay was not achieved. Nevertheless, all samples prepared were translucent, even those with the highest volume concentration of 2.5%.

The average intergallery distance was determined by means of X-ray scattering. In Figure 4, the scattering intensities of powders of the composites and of the pure filler are plotted against the 2-fold scattering angle θ.

From the 001 reflexes the intergallery spacing d can be calculated according to Bragg's law:

$$d = \frac{n\lambda}{2 \sin \theta} \qquad (3)$$

with n being the order of interference and λ the wavelength of the X-rays. The intergallery distance of the pure clay followed as 2.98 nm. By mixing the clay into the polymer the mean

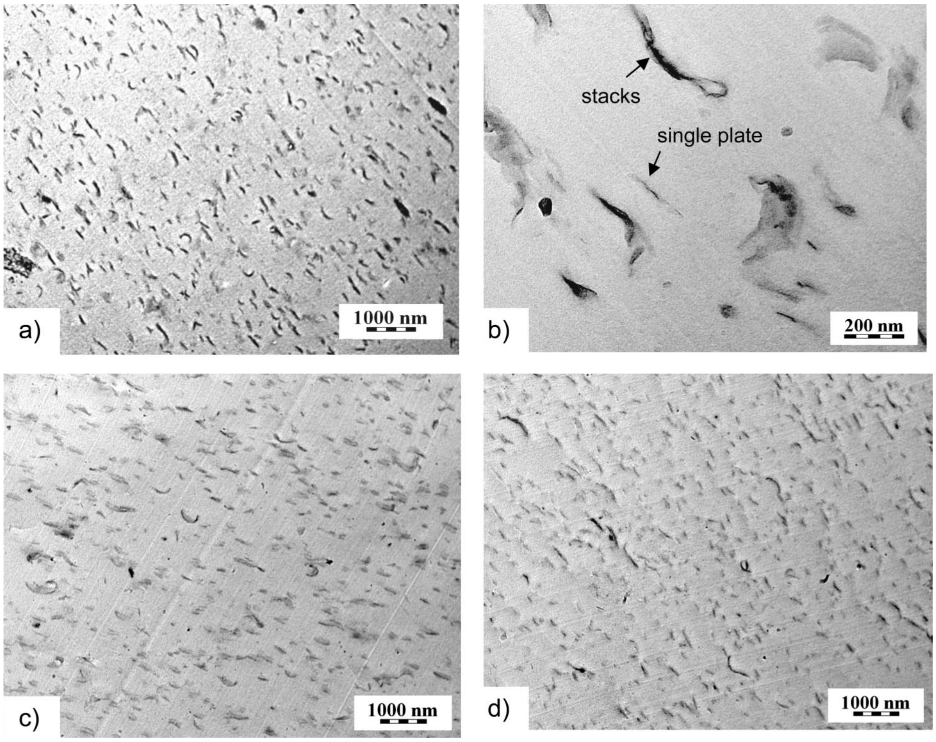

Figure 3. TEM analysis of PMMA 7N with 2.5 vol % nanoclay (a) medium and (b) high magnification, (c) PMMA 7 M with 2.5 vol % nanoclay, and (d) PMMA 7H with 2.5 vol % nanoclay.

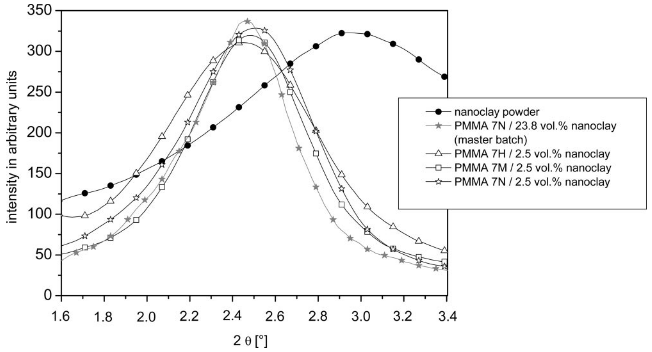

Figure 4. 001 reflexes of the XRD profiles of the nanoclay, the PMMA 7N/nanoclay masterbatch, and the composites of 2.5 vol % nanoclay each in PMMA 7N, PMMA 7 M, and PMMA 7H.

spacing of the platelet stacks increased to values between 3.52 and 3.58 nm for 2.5 vol % nanoclay in PMMA 7N, PMMA 7M, and PMMA 7H. However, these differences are in the range of the experimental error. Very interesting is the fact that there is no difference of the mean layer distance for the exemplarily shown PMMA 7N masterbatch with 23.8 vol % nanoclay after solution mixing compared to the composite diluted with pure PMMA 7N after melt mixing. To explain this finding, the mechanisms of intercalation and exfoliation of the clay in polymer composites according to Alexandre and Dubois[15] are taken into account. They state that an interaction between solvent and clay as well as between polymer and clay can lead to the increase of the intergallery distance and finally to an intercalation of the polymer chains between the platelets. The mean interlayer distance, as stated above, was increased from 2.98 to 3.58 nm. The radius of gyration of the different PMMA molecules is calculated to be 5.5−7 nm depending on the molar mass. Therefore, polymer chains would find sufficient space between the silicate layers in an extended conformation only, which is very unlikely. Hence, only the fraction of the molecules of low molar masses within the molar mass distribution may be able to intercalate.

Rheology

Tests of Thermal Stability, Linearity, and Stationarity. A precondition for reliable rheological measurements and their interpretation is the thermal stability of the material investigated. This property is particularly important, if long measuring times are applied.

By means of dynamic-mechanical experiments in the linear range of deformation the thermal stability of the samples was measured using time sweeps at frequencies close to the terminal region. The thermal stability is assessed via the storage modulus G', which is correlated to $M_w^{6.8}$ in the terminal regime. Samples are regarded to be stable as long as G' does not diverge more than ≈5% from its initial value. For the pure PMMA no change of the storage modulus within the stability limit even after 20 000 s at 183 °C was found. At the same temperature G' decreases with measuring time for all PMMA grades with 2.5 vol % clay, which can be interpreted by a molecular degradation (cf. Figure 5). The mechanism underlying this process is not clear up to now. With increasing molar mass the thermal stability decreases from about 20 000 s for PMMA 7N to about 10 000 s for PMMA 7H as matrix. As this is the lowest stability time measured for all materials investigated, the experiments were limited to that duration when samples with different matrices are compared.

In Figure 6a the results of two creep and creep-recovery experiments at a shear stress of 50 Pa are shown for the neat PMMA 7N to demonstrate the good reproducibility of the measurements. The creep compliance $J(t_{cr})$ increases with the creep time t_{cr} and reaches the terminal flow zone, which is characterized by a double-logarithmic slope of one. $J_r(t_0,t_r)$ grows with recovery time t_r, too, and reaches a stationary value $J_{r,\ s}(t_0)$ at longer times. Furthermore, a test at a creep stress of 20 Pa is shown in the same diagram. From the agreement of the curves at the two different creep stresses it can be concluded

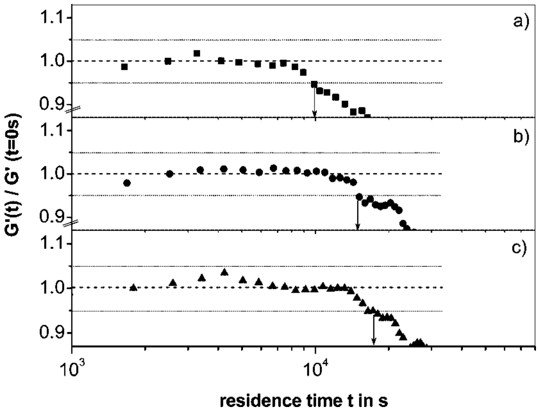

Figure 5. Relative change of storage modulus as a function of the residence time at 183 °C for (a) PMMA 7H ($T = 0.063$ rad/s), (b) PMMA 7 M ($T = 0.151$ rad/s), and (c) PMMA 7N ($T = 0.317$ rad/s) with 2.5 vol % nanoclay each.

that the response of the material is linear at least up to 50 Pa. The dependence of the recoverable compliance on the creep time t_0 is shown in Figure 6b for creep times of 1000, 2000, or 4000 s, respectively. There is a slight increase in $J_{r,s}$ for a creep time of 2000 s compared to 1000 s, indicating that the steady state in creep was not reached after 1000 s. The recoverable compliances $J_{r,s}(t_r)$ for the creep times t_0 of 2000 and 4000 s coincide. This means that at 50 Pa a creep time of 2000 s is long enough to determine the linear steady-state recoverable creep compliance J_e^0.

A similar test series was performed for the composite materials. In Figure 7a the data for PMMA 7N filled with 2.5 vol % nanoclay are presented. While the creep compliances of two measurements at 50 Pa can well be reproduced, small differences are found for the recoverable compliances which may be due to inhomogeneities of the particle distribution. In the following, curves as an average of two measurements will be discussed and analyzed. Similar to the unfilled materials all experiments on the composite materials are performed in the linear regime, indicated by compliances independent of the applied shear stress (Figure 7a).

In comparison to the neat polymer the creep time $t_0 = 4000$ s is not sufficient to reach J_e^0. This is shown in Figure 7b where J_r significantly increases with larger creep times t_0. The enhancement of t_0 by a factor of 2 from 4000 to 8000 s increases $J_{r,s}$ by a factor of 3. The reproducibility of the measurements is very good. These findings demonstrate the pronounced effect the filler has on the retardation times and the elasticity. Higher creep and recovery times cannot be applied due to the limitations in stability of the samples (cf. Figure 5). Although the steady state has not been reached, it is essential to note for the following discussion that the steady-state recoverable compliance J_e^0 is larger than or at least equal to the measured value $J_{r,s}(t_0 = 8000\ \mathrm{s})$.

Viscous and Elastic Properties of the Matrix Products. In Table 1 the viscosities and the elastic compliances of the three poly(methyl methacrylates) determined by creep and creep-recovery experiments in the linear range of deformation are listed.

If plotted double-logarithmically, the viscosities as a function of the weight-average molar masses follow a straight line with a slope of 3.6 as expected for homogeneous polymer melts (cf. Figure 8). This result demonstrates the reliability of the experimental method used and proves that the steady state and the linear regime have been reached. Furthermore, this relationship is another argument for an identical tacticity of the three polymer materials used, as, according to Fuchs et al.,[16] the viscosity of PMMA reacts very sensitively on this molecular parameter.

The linear steady-state recoverable compliances of the three PMMA are given in Table 1, too. They are particularly interesting insofar as the polydispersity factors are the same within the accuracy of the measurements (cf. Table 1) and, therefore, should show different values of the elasticity only if an influence of molar mass on this quantity would exist. Within the accuracy of the experiments J_e^0 is the same for all three samples, however. This result is in line with findings of Fuchs et al.[16] on anionic PMMA of narrow molar mass distribution, who found that the elasticity is independent of molar mass if it is higher by a factor of 3 than the critical molar mass for entanglements. The critical molar mass of PMMA is given by Fuchs et al.[16] as 40 kg/mol and by Fetters et al.[17] as 29.5 kg/mol; i.e., the molar masses of all the three samples investigated are distinctly higher (cf. Table 1).

Viscous and Elastic Properties in Dependence on the Filler Content. The creep compliances and the recoverable creep compliances of PMMA 7N filled with 1.7, 2.1, and 2.5 vol % clay are plotted in Figure 9. The creep compliance and, therefore, the zero shear-rate viscosity following from it show a marginal influence of the fillers, only. The recoverable compliances, however, significantly increase with the addition of the clay. The values are the larger the higher the filler content. The magnitude of the effect is very surprising if one takes the low amount of fillers into account. 1.7 vol % already leads to an enhancement of the elasticity by a factor of around 3 compared to that of the matrix. These differences are expected to become still more pronounced if longer creep times preceding the recovery process would be applied (cf. Figure 7b) and J_e^0 could be reached.

An interesting question rising from these findings is whether the very significant filler effects on elasticity are dependent on the molar mass of the PMMA matrix. In Figure 10 creep and recovery curves of PMMA 7N and PMMA 7 M filled with the same amount of 2.5 vol % nanoclay are compared.

The creep compliances of the composites based on PMMA 7 M are lower than that of the corresponding sample from PMMA 7N at the chosen temperature of 183 °C. This result is expected due to the higher molar mass of PMMA 7M. In parallel to that, the recoverable compliance is found to be smaller under the same experimental conditions. These results do not allow any reliable conclusion, however, as the retardation spectra of the two samples are different, and therefore, the recovery after a definite creep time does not start from the same state of deformation. Assuming the same elasticity of both samples, the spectra and following from that the time behavior should become equal if the viscosities and thus the molecular mobility of the two PMMA are matched. This can easily be done by choosing respective temperatures. As Figure 11 demonstrates, the creep curves of PMMA 7N and PMMA 7 M with 2.5 vol % of nanoclay become very similar if the lower viscous material is measured at 178 °C in comparison to the higher viscous one at 183 °C.

The recovery curves after a creep time of 4000 s are nearly identical indicating that the elasticity of the two filled samples is not much influenced by the molar mass of the matrix. PMMA 7H has a still distinctively higher viscosity. To adapt it to the one of PMMA 7 M a temperature of around 190 °C is necessary. This value is too high to grant a good enough thermal stability of the sample during the entire experiment (cf. Figure 5). In order to be able to include the high molar mass PMMA 7H in the investigations on the elasticity of nanoclay-filled systems, the temperatures as given in Figure 12 were chosen. To grant a reasonable thermal stability during the experiments the creep and recovery times were limited to 4000 s each. Figure 12 shows

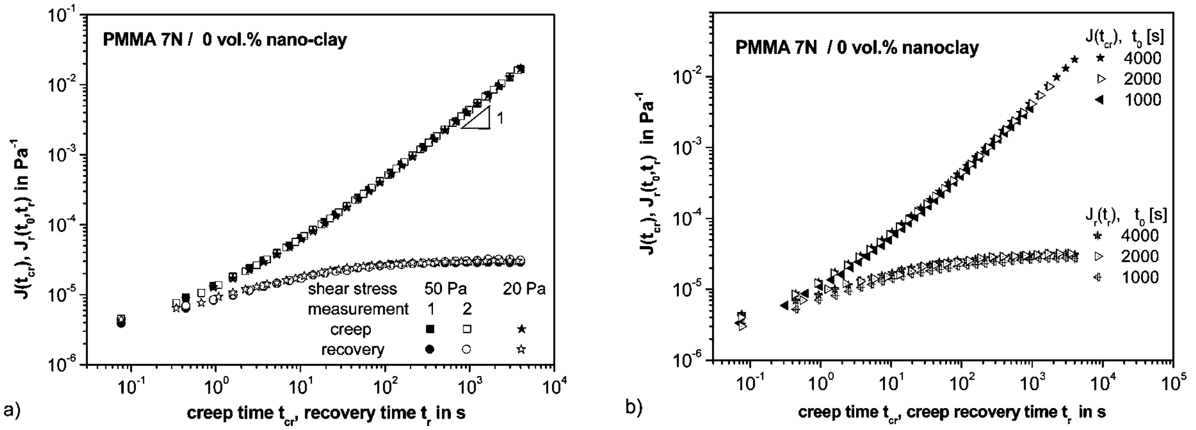

Figure 6. Creep and recoverable compliance of unfilled PMMA 7N at 183 °C (a) for two different shear stresses and a creep time t_0 of 4000 s (b) for different creep times t_0 and a shear stress of 50 Pa.

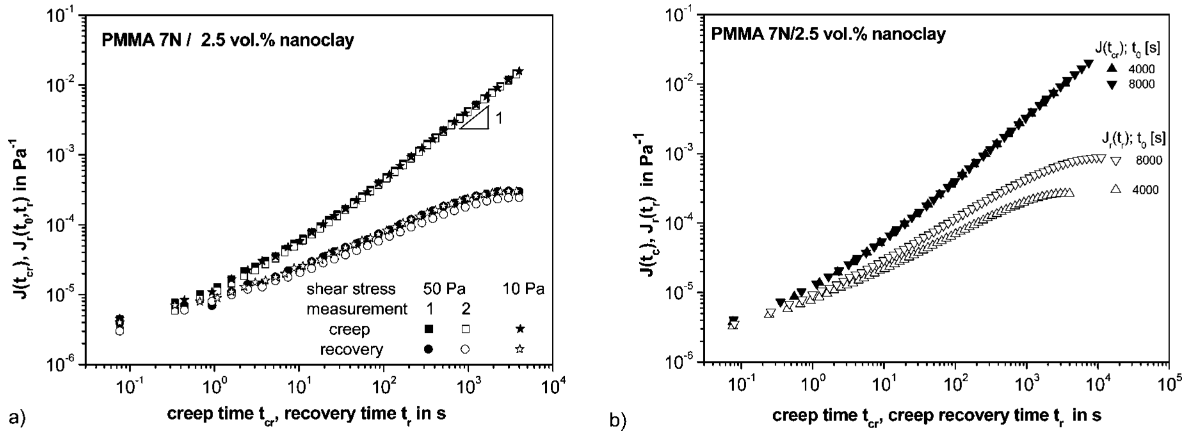

Figure 7. Creep and recoverable compliance of PMMA 7N filled with 2.5 vol % nanoclay at 183 °C. (a) Two runs at 50 Pa and the average of two runs at 10 Pa with a creep time t_0 of 4000 s. (b) Dependence on creep time t_0 at a shear stress of 50 Pa.

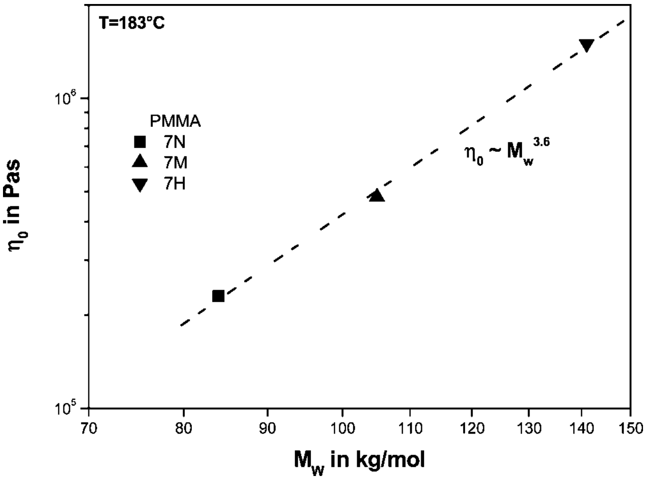

Figure 8. Zero shear-rate viscosity as a function of the weight-average molar mass. $T = 183$ °C.

that the creep and recovery curves of the three samples coincide within the accuracy of the measurements, supporting the finding of Figure 11 that the elasticity of PMMA filled with 2.5 vol % nanoclay is not dependent on the molar mass of the matrix.

Discussion

The rheological results on the three PMMA matrix products agree with those well-known from other homopolymer melts. They demonstrate the reliability of the experimental method

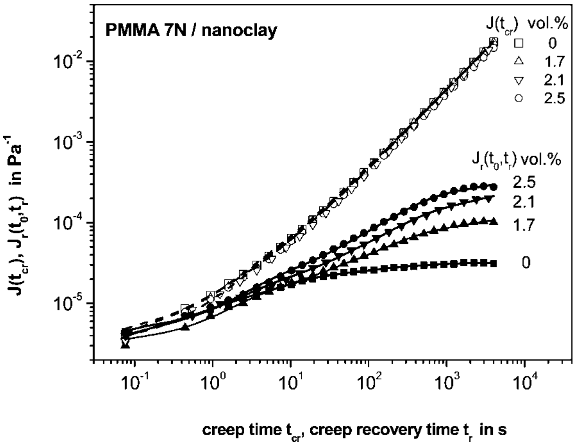

Figure 9. Comparison of the creep and recoverable compliances at 183 °C and a shear stress of 50 Pa with a creep time t_0 of 4000 s for PMMA 7N nanocomposites of different filler fractions.

used. Worthwhile discussing are the findings on the filled products. Taking the electron micrographs into consideration, it is obvious that a good dispersion of the filler particles has been obtained for all samples. Although two-dimensional, it can be concluded from the pictures that a continuous network built up by the nanoclay is not very probable even at the highest concentration of 2.5 vol %. This conclusion is consistent with the existence of zero shear-rate viscosities as a network should result in a yield stress and following from that in a viscosity increase at small stresses. Nevertheless, some kind of interaction

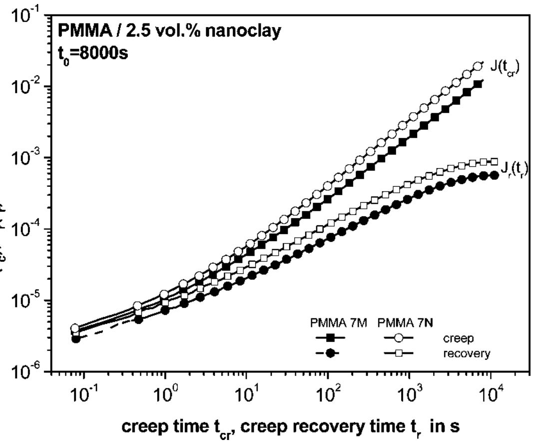

Figure 10. Comparison of the creep and recoverable compliances for nanocomposites containing 2.5 vol % nanoclay using PMMA 7N and PMMA 7 M as a matrix. The measuring temperature was 183 °C; a creep time t_0 = 8000 s was applied.

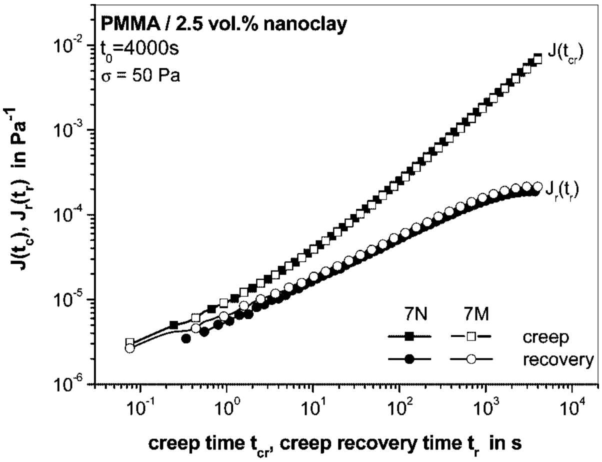

Figure 11. Comparison of the creep and recoverable compliances for nanocomposites containing 2.5 vol % nanoclay using PMMA 7N and PMMA 7 M as a matrix. The measuring temperature was 183 °C for PMMA 7 M and 178 °C for PMMA 7N, respectively. A creep time t_0 = 4000 s was applied.

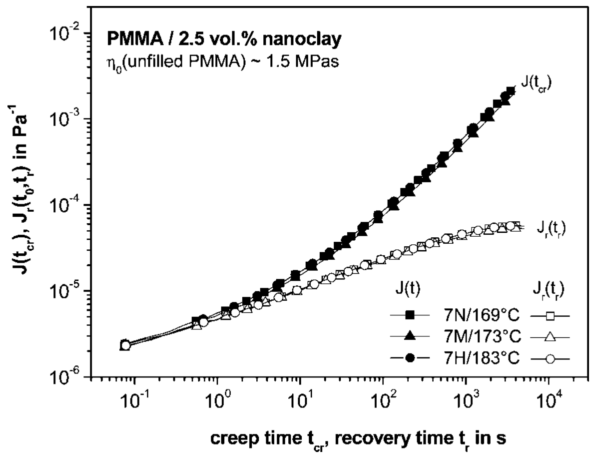

Figure 12. Comparison of the creep and recoverable compliances at a shear stress of 50 Pa with a creep time t_0 = 4000 s for PMMA nanocomposites of different matrix polymers at adapted temperatures.

between the filler particles and the polymer molecules has to be discussed in order to interpret the viscoelastic properties measured. The bulk viscosity of the composites as expressed by the third term of eq 2 is dominated by that of the matrix. From this finding it could be concluded either that there is no effect of the fillers on the overall mobility of the polymer molecules or that the influence of an interaction between the particles and the macromolecules is very small.

However, an interpretation of the elasticity measured by the recoverable creep compliance in the linear range of deformation and dominated by the second term of eq 2 has to postulate an interaction between the nanoclay particles and PMMA molecules, as a remarkable increase of this quantity was observed for the filled samples investigated in this paper. This result is in contrast to other elastic quantities of filled polymers like the extrudate swell or the recoverable portion of elongational flow. For the extrudate swell a decrease is obtained by adding fillers, and the same effect is observed for the recoverable part of the elongation of polymer melts.[18] These findings are generally explained by the simple picture that nondeformable particles replace flexible molecules, thus reducing the amount of elasticity inherent to a material. This interpretation apparently does not hold for the results presented. As the filler content is small an elasticity not much dependent on the filler concentration could be expected, but not an increase by an order of magnitude. A very obvious difference regarding the experimental conditions, however, is that the measurements of extrudate swell and recoverable elongation are performed in the nonlinear regime whereas the creep-recovery experiments presented here are strictly linear.

Therefore, a model is postulated on the basis of an interaction between molecules and fillers. If one assumes that the molecules close to the filler surface are attached to it by physical adhesion forces, their restricted mobility becomes obvious. Thus, disentanglement effects of these molecules are apparently hindered, leading to higher retardation times and strengths than in the case of molecules not interacting with the particle surfaces. This change of the retardation spectrum easily explains the elasticity increase. Enhancing the particle concentration should lead to a higher overall number of molecules attached to the particles, resulting in the increased elasticity found in the experiments performed. This effect is expected to be the more pronounced the lower the elasticity of the matrix as in such a case the additional elasticity due to interactions between molecules and particles may significantly contribute to the overall elasticity. Since the elasticity of the matrices is relatively low because of the narrow molar mass distributions, the PMMA samples of this paper are particularly well suited for investigating the influence of fillers on elasticity. Of course, the substitution effect of the particles generally lowering the elasticity of filled polymers has to be taken into account, too. The findings of an increase in elasticity for the PMMA/nanoclay systems can be explained by assuming that the growth of elasticity due to interactions between the polymer molecules and the filler surfaces overrides the substitution effect. According to this model, one would expect that the filler elasticity runs through a maximum as a function of filler content. Filler concentrations in this range were not applied in this work, however, as it is nearly impossible to reach a steady state during the stability window of the samples.

The apparent discrepancy between the filler effect enhancing the recoverable elastic compliance as obtained by the creep-recovery experiments of this paper and the decrease of the recoverable portion of the elongational flow[18] can find an explanation by this model, too. Whereas the recovery experiments described are performed in the linear range of shear, the recoverable elongation was measured in the distinctly nonlinear regime. It is not unreasonable to assume that the interactions between molecules and particle surfaces become weaker under the higher stresses applied in the nonlinear regime as they may

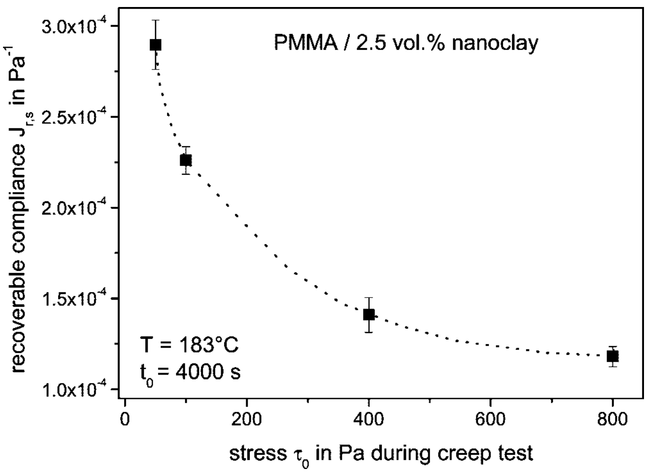

Figure 13. Recoverable shear compliance as a function of applied shear stress.

counteract the attraction forces. This assumption is supported by the results presented in Figure 13. It is clearly shown that the recoverable compliance of the PMMA 7N filled with 2.5 vol % nanoclay decreases as a function of the previously applied creep stress. The growth of the stress by a factor of 16 reduces the elasticity by a factor of 3. But even at the highest stress applied the value of the elastic compliance is still larger than the linear value of the unfilled material (cf. Table 1). This finding indicates that some kind of interaction between the matrix molecules and the particles is still existent even under the nonlinear conditions chosen.

The time dependence of the recovery is governed by the viscosities of the matrices. This can be concluded from the fact that identical recovery curves are obtained if the viscosities are adapted by choosing the respective temperatures. This experimental finding gives a hint to an elasticity of the nanoclay filled PMMA which is independent of the molar mass of the matrix. Such a conclusion is not in contrast to the model proposed as the chemical nature of the three PMMA used is the same and their coil diameters are not much different, implying similar adhesion forces and numbers of molecules which interact with the particle surfaces.

Surprising at a first glance is the experimental result that the filler content only weakly influences the viscosity. A very qualitative explanation can be given by the following consideration. In a rough approximation it can be assumed that the overall viscosity of the filled system is composed of that of the matrix molecules and that of the molecules attached to the particle surface. Their contribution is small, however, as long as the particle content is low. Assuming a logarithmic mixing rule, it is obvious that the viscosity of the composite is governed by that of the matrix as the percentage of the molecules interacting with the particle surfaces is relatively small even for the highest chosen concentration of 2.5 vol %.

Conclusions

It has been demonstrated that creep-recovery experiments are a very sensitive method to determine elastic properties of polymer melts. On three PMMA samples of identical tacticity and of comparable polydispersity but different molar masses, it could be shown that for this class of polymers the elasticity is independent of the molar mass as it is reported for other homopolymers in the literature, too.

Small amounts of nanoclay significantly increase the elastic compliance of PMMA measured in the linear range of deformation. This growth in elasticity is not due to the formation of a network proven by transmission electron micrographs and the existence of a zero shear-rate viscosity. An enhancement of elasticity by a factor of up to 10 is measured for a volume concentration of 2.5% although a significant exfoliation of the nanoclay is not found and the intercalation of polymer molecules is very limited. The recoverable creep compliance becomes smaller with decreasing filler content. The molar masses of the matrices used influence the time dependence of the recovery, but the elasticity seems to be unaffected. This conclusion becomes obvious from the experimental finding that the time dependencies of the recovery can be explained by adapting the temperatures, only.

The remarkable growth of elasticity with the addition of fillers measured by the linear recoverable shear creep compliance is in contrast to the decline of elasticity found in the literature for the recoverable portion of elongation even at low concentrations of nanoclays. An explanation can be given by the highly nonlinear deformation applied in elongation. This conclusion is supported by creep experiments under nonlinear shear which clearly demonstrate that the recoverable compliance becomes smaller with growing stress.

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