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Comparative rheological studies of polyamide-6 and its low loaded nanocomposite based on layered silicates

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Abstract We study some rheological properties for polyamide-6 (PA-6) and a low concentrated clay nanocomposite melt based on polyamide-6 and montmorillonite. Simple shear experiments, carried out for both the neat system and nanocomposite at two different temperatures, include start up shear flows, stress relaxation after cessation of steady flow and oscillatory shear. The dynamic data for the neat PA-6 matrix differ markedly from that of the nanocomposite system, even if it has very low nanofiller concentration. Thermal stability of the PA-6 matrix imposed many restrictions on rheological studies of our systems. Therefore an experimental window was established via rheological and thermal characterization of the

materials, wherein the polymer matrix was confirmed to be thermally stable. The relaxation spectra for both polymer systems were determined from linear dynamic experiments using the Pade'-Laplace procedure. A rough estimation of nanocomposite volume fraction at percolation allowed us to attribute the occurrence of extra (relative to the neat polymer) Maxwell modes observed for the nanocomposite to the formation of a particulate network above the percolation threshold.

Keywords Nanocomposite layered silicates · Pade'-Laplace method · Relaxation spectra · Maxwell modes · Percolation threshold

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Introduction

The layered silicate nanocomposites are made of highly anisotropic layered particles dispersed in polymer matrix. The particles have thickness of 1–5 nm and the sizes in the other two dimensions of few hundred nanometers. Structurally, a well-ordered multilayered stack of polymer and the layered platelets are identified as *intercalated nanocomposites* while randomly distributed platelets in the polymer matrix are termed *exfoliated nanocomposites* (Krishnamoorti and Giannelis 1997). The advantages of this type of nanocomposites include more reinforcement at lower filler contents and hence better mechanical and barrier properties as compared to that for neat polymers (Garcés et al. 2000; Alexandre and Dubois 2000).

Krishnamoorti et al. (1996) and Giannelis et al. (1999) have recently discussed the static and dynamic properties of polymer/layered silicate nanocomposites in relation to their structural characteristics. Krishnamoorti and Giannelis (1997) also reported the rheology of poly(ϵ -caprolactone)/montmorillonite and nylon-6/montmorillonite. The major observation of this study was the deviations observed for nanocomposites in low frequency region from the standard power law dependencies known in flow region for the dynamic moduli of polymer melts. This was then explained in terms of structure formation in the polymer matrix owing to uniform distribution of the clay platelets. Using a simple phenomenology, Ren et al. (2000) correlated the critical weight fraction for structure formation with the number of silicate layers per tactoid for

intercalated nanocomposites. Fewer studies are published so far in the field of rheology of the nanocomposites for both the intercalated or exfoliated cases. Most of these studies focus on low amplitude dynamic measurements for different polymer systems and at various clay loadings. Apart from qualitative explanations, no direct evidence has been established which relates the deviations in dynamic moduli to the microstructure due to the clay dispersion. Also, the rheology of the neat polymer matrix, PA6, including its dynamic, steady shear properties and its quantitative analysis, is currently barely known in spite of versatility of its applications. The foremost reason for that are the experimental difficulties associated with the characterization of this polymer. To the best of our knowledge, we address this problem for the first time within experimental constraints and provide with important rheological results depicting the rheology of the neat polymer and its nanocomposite.

The melt state rheological behavior of nanocomposite systems is mostly reminiscent of that found for flocculating suspensions, polymers/elastomer compounds with active fillers, and for nematic liquid crystalline polymers. One can find a detailed experimental and theoretical analysis of flocculating suspensions in publications by Leonov (1990) and Coussot et al. (1993, 2002). These studies discussed the interactions between the particles and a liquid matrix and between the particles themselves. Vinogradov et al. (1972) discussed a particulate network formation of active fillers with spheroidal particles above their critical volume loading (percolation threshold) for filled polymers or elastomers. Krishnamoorti and Giannelis (1997) also discussed similar behavior of nanocomposites with liquid crystalline polymers and ordered block copolymers.

These studies showed that the network formation due to the particle and other interactions in the nanocomposite system are vital for determination of their final properties. A prominent effect of such interactions may be revealed in comparative studies of the relaxation mechanism(s) of a nanocomposite system against its neat polymer. The relaxation mechanisms described by the relaxation spectra contains the details of material properties, which depend on the molecular and particulate structures of neat polymer and filler in nanocomposites. To the best of our knowledge, such studies have not been yet reported.

The present paper, focused on shear rheological experiments in linear and nonlinear region of deformations, makes comparative studies of a highly interactive nanocomposite system of polyamide-6/montmorillonite with very low ($\sim 1\%$ of volume) loading, and a neat polyamide-6 with the same molecular grade as used in the nanocomposite matrix. Unlike many previous papers (Krishnamoorti and Giannelis 1997; Ren et al. 2000) where the comparative studies were performed

for dynamic ($G'(\omega)$ and $G''(\omega)$) characteristics for many compositions, we study here only one, low concentrated nanocomposite as compared with the PA6. This provides us with an opportunity to interpret the data, obtained in our experiments, in terms of discrete relaxation spectra.

Our shear experiments present the transient stress in a start-up flow under various constant shear rates and the stress relaxation after cessation of steady shear flow. In the low amplitude dynamic experiments, even at low volume loading of the filler, we observed in the low frequency regime a considerable deviation between the properties of nanocomposite and the neat polymer. The dynamic data are further used to find the relaxation spectrum for the two polymer systems at two different experimental temperatures and make a comparison between the two. To determine the relaxation spectra, we use the well-posed Pade'-Laplace procedure whose application and methodology has been described in detail for stress relaxation experiments by Fulchiron et al. (1993) and for dynamic measurements by Simhambhatla and Leonov (1993).

Experimental

Materials Two polymer systems, polyamide-6/montmorillonite ($\sim 1\%$ filled by volume) nanocomposite and the neat polyamide-6 (PA6) were used in the present study. Both the filled and unfilled polymers were generously provided by Ube Industries Ltd. Japan. The weight average molecular weight (as indicated by the company) of the polymer matrix in both the polymers is approximately 22,000. It was reported to us that the nanocomposite prepared was in-situ polymerized. Initially the montmorillonite was cation exchanged with amino acid cations, typically done to render the hydrophilic platelet surface organophilic. The monomer, ϵ -caprolactam was polymerized in presence of the surface modified filler.

Rheological testing The material for testing was initially kept under vacuum at 80 °C for 12 h. The moisture content in the material was carefully monitored below 0.1%. The material was then compression molded at 250 °C into the disk shape testing samples of diameter 20 mm and height 2 mm.

The rheological behavior of the samples was tested on RMS 800 (Rheometrics Mechanical Spectrometer 800). In this instrument, the lower fixture (plate) is fixed, while the upper fixture (cone) moves down towards the plate, with a d.c. motor rotating the plate. To obtain the maximum possible frequency range we worked with both the transducers of high range (1.5–2000 g cm) and low range (0.15–200 g cm).

After a sample was loaded into the rheometer, it was initially pre-sheared at a shear rate of 0.5 s^{-1} for 90 s. Variations in pre-shear time did not affect the results of measurements, meaning the pre-shearing history was erased. After preshear, the sample was allowed to rest for enough time before starting either steady or dynamic measurements.

The transient shear testing under constant shear rate was performed using cone and plate geometry. The used cone angle was 0.1 rad and the plate diameter 20 mm. The study was done at five different shear rates. Typically the shear rate was held for nearly 5 min, and then the flow was ceased. The sample was allowed to relax for about 3 min. The same shear rate was imposed on the

sample once again and a similar second cycle of shearing was performed.

Time sweep experiments were performed to measure G' and G'' against time at commanded strain and constant frequency in simple shear. We used constant frequencies of 1 rad/s, 2 rad/s, and 10 rad/s and the sinusoidal strain of 1.5% each time. This in effect gives a measure of G' and G'' values at corresponding frequencies and the strain applied in dynamic frequency sweep experiment. The experiments were performed on RMS-800 using plate and plate geometry.

The small amplitude dynamic measurements were carried out using parallel disk geometry with 20 mm disk diameter. The thickness of sample in cone-plate geometry was typically 0.05 mm and it was nearly 1.2 mm in case of disk-disk geometry. The transient shear measurements and the small amplitude dynamic measurements were performed at 250 °C and 260 °C. The rheological properties were reproducible for different fresh samples tested under the same conditions within a certain time frame at the test temperatures.

Thermal characterization of samples by DSC DSC analyses of both the filled and neat systems were made to find the thermally stable temperature range for rheological characterization of both the polymer systems. The samples were tested in the temperature range 30–350 °C with a heating rate of 10°/min. Nearly 10 mg sample was used for the test. Apparently the study also reveals difference in melt state behavior of the polymers under study at the prescribed melting points.

Results and discussion

Transient shear experiments

Upon shearing, the shear stress in the samples displayed an almost instantaneous overshoot, which was followed by an almost immediate decrease in its value (Fig. 1) which remained steady in the later duration of the experiment. No stress overshoot was observed for shear rates of 0.1 s⁻¹ or lesser magnitude. This type of behavior is common for many observations for either neat or filled polymers. After cessation of the steady shear flow, the shear stress almost immediately fell down to a negligibly small value. This indicates the fast relaxation of the polymer sample. The minimum stress level after relaxation of the sample was either very low or nearly zero (Figs. 2 and 4b). When it was observed to be negative (Fig. 4a), it was due to the insensitivity of the transducer to such low levels of stresses in the polymer system. As seen in Fig. 1, the stress in the system increases with increase in shear rate. In the second cycle, the shear stress again showed a similar behavior with nearly the same or relatively small value of the overshoot. This is illustrated in the typical stress relaxation cycle shown in Fig. 2. The relaxation tail observed could be due to the high modulus of the polymer material.

Flow curves were obtained using the transient shear steady data at the two temperatures used. The steady values of shear stresses were plotted against respective shear rates. These dependencies are shown in Fig. 3.

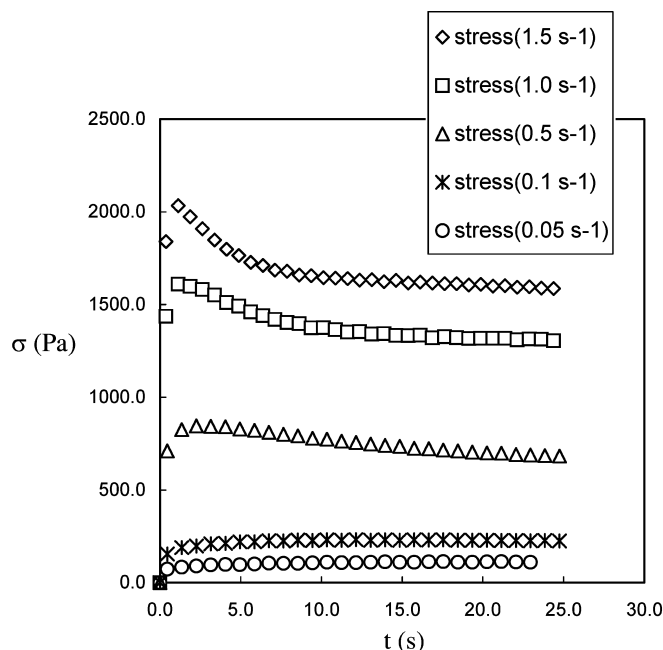


Fig. 1 Stress growth during transient shear experiment of PA-6/clay nanocomposite at constant shear rates and constant temperature of 250 °C

Material instability of polymer systems

The overall duration of the experiment was purposely set within a 20-min time frame. There was a following reason for that. The long time stress growth experiment (Fig. 4a) performed at constant shear rate showed an unstable material behavior. The shear stress (and viscosity) of the material, behaving initially similar to that described above till approximately 20 min, then started increasing. After a sufficiently long period of time (nearly 45 min)

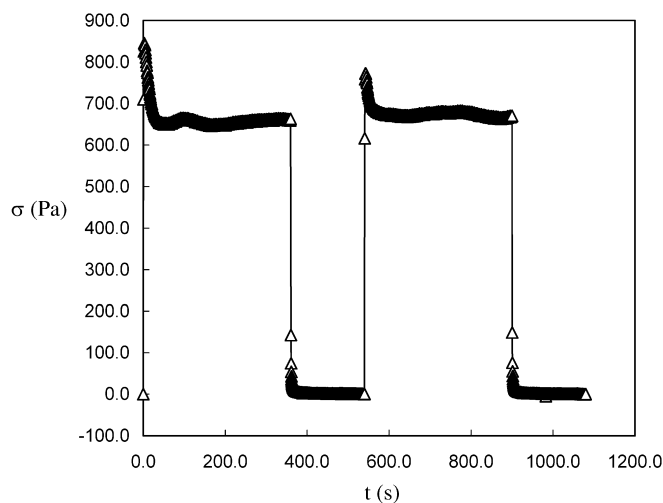


Fig. 2 Stress growth and relaxation cycle for PA-6/clay nanocomposite at constant shear rate of 1.5 s⁻¹ and 250 °C temperature

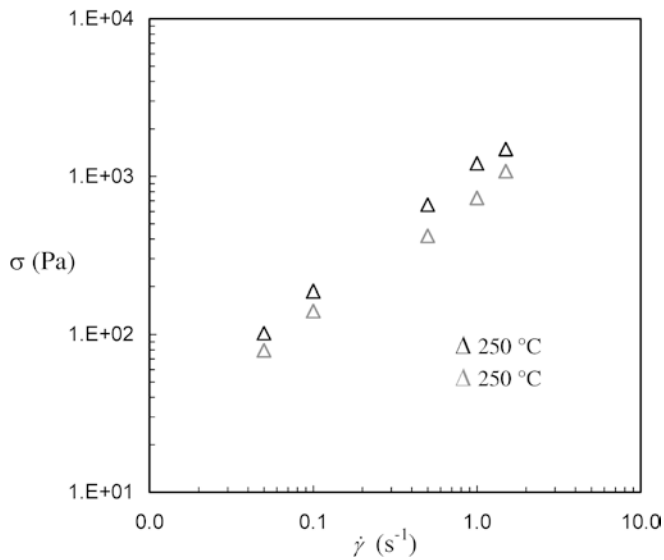


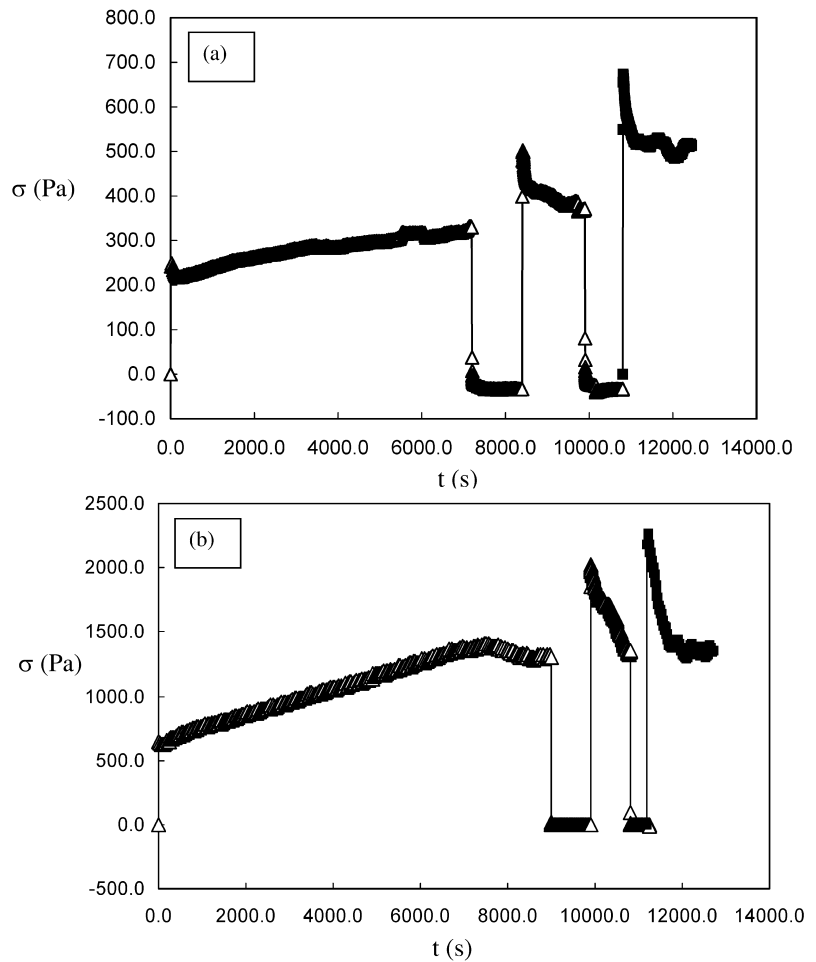
Fig. 3 Flow curves for PA-6/clay nanocomposite at 250 °C and 260 °C

it again showed a decrease in value but the data observed were very scattered. This could be an indication of material degradation. At this point, material inspection showed visible color change from initial white opaque to final dark brownish opaque. This color change was not noticed within the time frame, 20 min, established for the experiments. To verify the material instability behavior, a similar experiment was performed for the neat polyamide-6 and similar result was obtained (see Fig. 4b). Hence, to avoid any ambiguity, the operating window for all type of experiments was set within the time frame in which the material shows relatively stable behavior. Also it was observed that the instability effect increases with an increase in the shear rate. The instrument sensitivity also imposed a constraint on the lowest shear rate used in our experiments.

Thermal Characterization

The transient shear data were obtained at two different temperatures, 250 °C and 260 °C. The trend in the

Fig. 4a,b Stress vs time for:
a PA-6/clay nanocomposite;
b PA-6 showing instability of the polymer at long time exposure to high temperature (250 °C)



behavior of both the systems at these temperatures was observed to be nearly similar. We could not obtain thermally stable data at and above 270 °C, while an incomplete melting of crystallites and hence significantly high stresses in the sample were observed at 240 °C. This type of behavior was further clarified using DSC experiments.

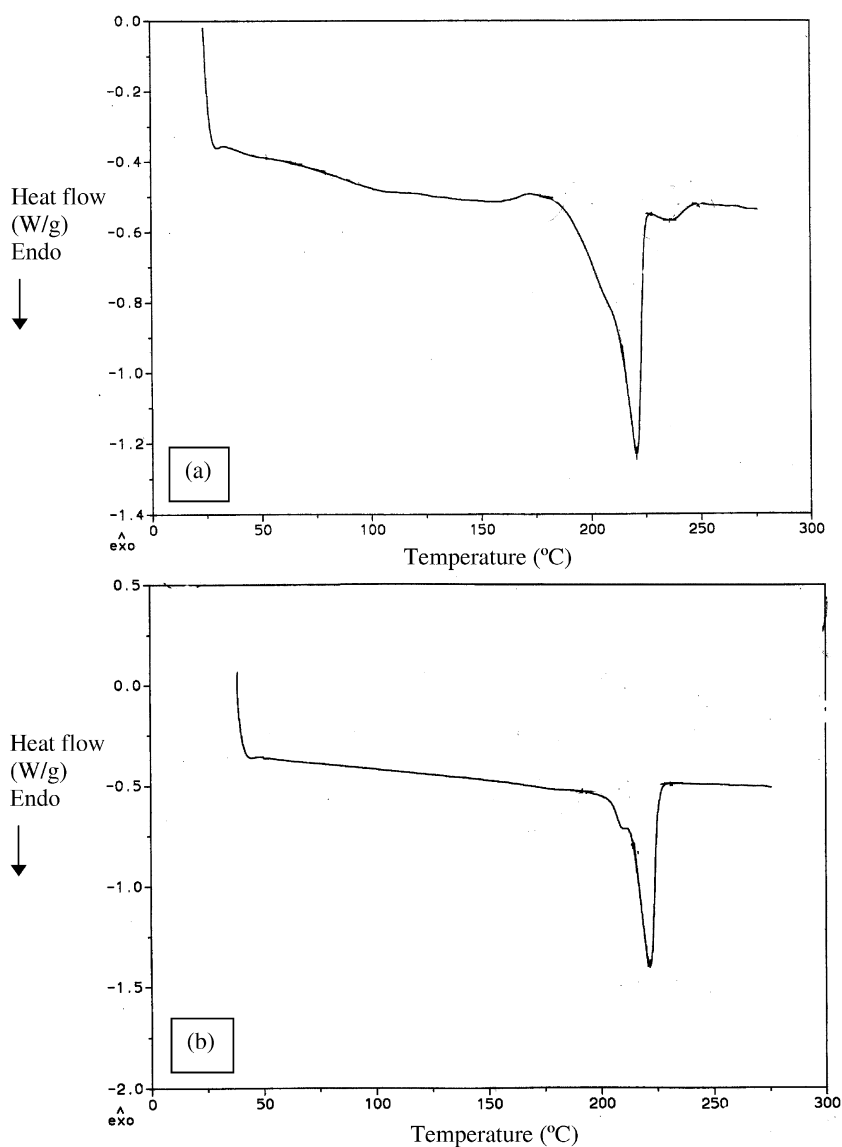
At 240 °C, the values of recorded dynamic moduli were very high as compared to that at 250 °C. It was then assumed that the material might not have been completely melted at 240 °C. DSC heating scan (Fig. 5a) at the same temperature supported the assumption. It demonstrated a small endothermic peak after the melting peak at 230 °C in the temperature range from 231 °C to 245 °C. Such a peak was not observed for the neat polyamide-6 material (Fig. 5b). Liu et al (1999) also reported similar DSC results. They observed a difference

between the crystal structure and crystallization behaviors of the nylon-6/clay nanocomposites and nylon-6. Nylon-6 has a more stable α crystalline form rather than the γ form. They showed that nylon-6 has only one melting peak corresponding to the α crystalline form but the nanocomposite system has two melting peaks. The high-energy peak there corresponded to the α form while the low energy peak of the γ crystalline form was attributed to the clay incorporation.

Time sweep experiments

In these experiments the percentage strain and also the frequency of measurement was held constant and the behavior of moduli vs time was observed. Ideally, the value of moduli observed at a given frequency in

Fig. 5a,b DSC scan of: **a** Polyamide-6/clay nanocomposite; **b** neat PA-6



frequency sweep experiments should match with the moduli observed in time sweep experiments under given deformation.

From Fig. 6, it is seen that the moduli are nearly time independent under observed strain and frequency. The values observed in both time sweep and frequency sweep experiments are nearly in agreement with each other, which confirms the validity of oscillatory measurements. In these experiments again, the period of observations was limited by instability of the material at high temperatures and long time duration.

Some of the representative comparisons are shown in Table 1.

Dynamic shear experiments

The dynamic properties of filled polymers are important for evaluating their structure. Incorporation of fillers greatly influences the nature of material response on forces. Vinogradov et al. (1972) first demonstrated that the rheological response of filled polymers with active filler markedly differs from that of the unfilled systems. With increase in filler loading the effects are usually prominent. Near a critical value of filler loading, attributed to the percolation threshold, the particle-particle and particle-polymer interactions dominate to form a secondary network structure, which breaks down under loading. These phenomena can be studied by dynamic measurements. For the polymer liquids, the

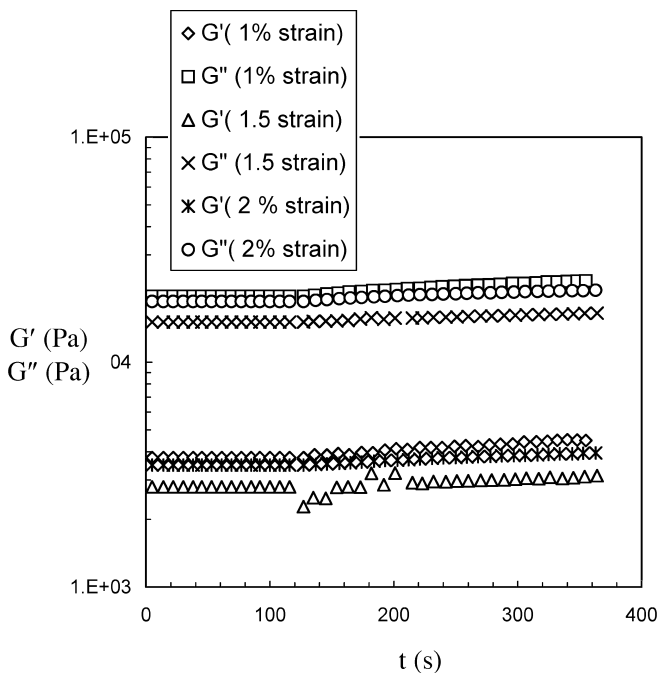


Fig. 6 Time sweep plots. The storage moduli and loss moduli of PA-6/clay nanocomposite are measured under constant amplitude of deformation and frequency and at 250 °C

Table 1 Comparison of storage moduli (G') and loss moduli (G'') obtained for PA-6/clay nanocomposite from frequency sweep and time sweep experiments at same frequency and commanded strain at 250 °C

Frequency (ω)(rad/s)	Commanded strain (γ)(%)	Frequency sweep		Time sweep	
		G' (Pa)	G'' (Pa)	G' (Pa)	G'' (Pa)
1	1.5	1.25×10^4	2.7×10^4	1.30×10^4	2.86×10^4
10	1.5	7.82×10^4	1.45×10^5	8.02×10^4	1.53×10^5

well-documented behavior of storage G' and loss G'' moduli in the low frequency terminal zone is: $G' \sim \omega^2$, $G'' \sim \omega$. In contrast, the more complicated behavior of fluids with yield in the terminal zone shows that $G' \gg G''$, with G' being nearly frequency independent.

The critical volume of filler loading defined in terms of percolation threshold depends upon the number of silicate platelets per tactoid (stack of platelets dispersed in the polymer matrix) and the aspect ratio of the platelets. One can perform simplified calculations to find the critical volume fraction of silicates: $\varphi_{per} = (6/\pi)(d/B)\varphi_*$. Here φ_* is the critical volume fraction of spherical particles at percolation, d is the average thickness of stacks of platelets, and B is the platelet length (width). This formula, similar to that which has been proposed in the literature by Ren et al. (2000), assumes that particles of non-spherical shape organize a “particulate network” as soon as their hydrodynamic spherical volume concentration (calculated with the radius equal to $B/2$) reaches the value of φ_* . Theoretical calculation of φ_* performed under (implicit) assumption that particle/particle interactions are highly dominant resulted in the value $\varphi_* \approx 30\%$. For the suspensions of spherical particles in polymeric matrices with highly prevailing particle/polymer interaction, the critical value of φ_* at percolation is expected to be considerably less. This is because a lot of macromolecules are involved in this case in the formation of a “knot” in the particulate network. For example, Vinogradov et al. (1972) reported the value $\varphi_* \approx 15\%$ for a rubber compound filled with carbon black particles that has dominant particle/polymer interaction. Judging by a good exfoliation, the silicate particle/macromolecule interaction is also dominant in our system.

For our system, the average value of platelet length (width) confirmed by the company-producer (see also Vaia 2000) is: $B \approx 160 \pm 30$ nm, with the medium platelet thickness $d \approx 3$ nm (ranging from 1 to 5 nm). Thus the average value of the volume fraction of the nano-filler at percolation threshold is

$$\begin{aligned} \varphi_{per} \% &\approx 0.036 \varphi_* \% \approx 0.036 \cdot (15 \leftrightarrow 30) \% \\ &\approx (0.54 \leftrightarrow 1.08) \% \end{aligned}$$

Because of the strong interaction of silicate platelets with PA6, we can expect that the ϕ_{per} for our system is close to the lower value of the above estimate. It means that the volume filler loading $\sim 1\%$ used for our nano-composite is (considerably) greater than the critical value of ϕ_{per} evaluated above.

It should also be mentioned that the particulate network of nanoparticles/polymer formed above the percolation threshold, especially with low values of ϕ_{per} , could by no means be treated as rigid. This is because the particles of nano-size are the subject of the rotational and translation Brownian fluctuations, whose characteristic time scale depends on the viscosity of matrix. Therefore the approximation of the contribution of fluctuating particulate matrix by a rigid behavior with "yield" might be only considered as very rough.

The slopes of G' and G'' in the terminal zone were estimated for Polyamide-6/clay nanocomposite ($\sim 1\%$ filled by volume) at frequencies below 0.1 rad/s. The PA-6 nanocomposite showed unusual terminal behavior with power-law dependencies for G' and G'' having much smaller slopes than the common ones 2 and 1, respectively. We found that $G' \sim \omega^{1.11}$ and $G'' \sim \omega^{0.84}$. One can speculate that this behavior is caused by the presence of fluctuating particulate network discussed above. The observed change in the behavior was more pronounced for G' than for G'' . Such a non-terminal flow behavior has been observed in filled polymer systems exhibiting yield phenomena, only in the case of actively interacting filler and polymer and for dynamic regime controlled by much larger length scales (i.e., lower frequencies) than those observed in this study. The deviations from the typical homopolymeric behavior in these systems have been observed in the literature at relatively high filler loadings. Non-terminal low-frequency rheological behavior has also been observed in ordered block copolymers and smectic liquid-crystalline small molecules. It has been suggested that undulations and defects in layers might contribute to the low-frequency viscoelastic response in layered block copolymers. Larson et al. (1993) demonstrated that the low-frequency response in the case of smectic small molecules and short ordered block copolymers is due to the long-range domain structure and the presence of defects.

One can imagine that, even in the exfoliated system, there would be domains of platelets with nano-size thickness oriented in the preferred direction (say, parallel to the flow direction). This orientation happens because the lateral dimensions of the platelets range from 100 to 1000 nm whereas their thickness from 1 to 10 nm, depending on whether there is a single platelet or their stack. The attachment of polymer chains to the platelets also plays important role in this orientation. The presence of such ordered/disordered structure embedded in the polymer matrix may be a reason for the low-frequency behavior of these nanocomposites.

Krishnamoorti and Giannelis (1997) have reported similar results for layered silicates systems in polyethylene oxide matrix. Their results also show that at the very low shear rates accessed, these nanocomposites exhibit such a low-frequency behavior that both G' and G'' are almost independent of frequency. This behavior, termed as "pseudo-solid", was clearly observed for the PEO/clay composites with filler loadings greater than 3%. Solid-like responses of filled polymer systems with appearance of 'yield' have been attributed to strong interactions between polymer and filler (e.g., see Agarwal and Salovey 1995).

Comparison of plots for storage and loss moduli vs frequency for neat PA6 and the nanocomposite material is presented in Fig. 7. The difference in behavior of these two materials, shown here is quite obvious. The low-frequency, terminal region of the nanocomposite gives a hint of the presence of apparent yield even at the volume filler concentration of $\sim 1\%$. With increase in filler loading, one can expect to observe the prominent yield behavior at comparatively very low concentration to that of the particulate filler loadings. The typical viscoelastic nature of neat polymer is evident from Fig. 7, which showed that $G' \sim \omega^{1.8}$ in the low frequency terminal region. The modulus of the neat polymer is very high. Hence at high frequencies the storage moduli of both the materials are quite close to each other. This is also seen from Fig. 7, which shows remarkably comparable loss modulus at higher frequencies for both the materials. At low frequencies the slope of the neat polyamide-6 is more tending towards the expected value of 1 (for linear polymers), as against 0.84 for the nanocomposite.

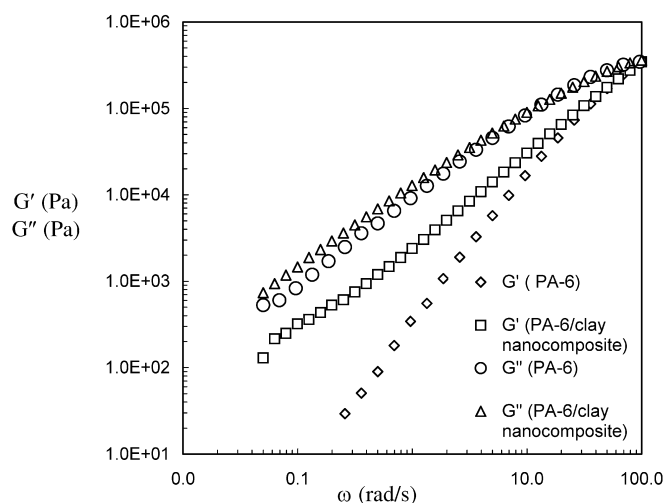


Fig. 7 Comparison of storage and loss moduli of neat PA-6 and PA-6/clay nanocomposite. Data measured at 250 °C

Relaxation spectra for polyamide-6/montmorillonite nanocomposite and neat polyamide-6

As compared to the homopolymers, extra long time, linear relaxation modes are observed with multiphase polymers capable of forming network structure or phase separation. Many numerical procedures have been developed to date in order to determine the relaxation time spectrum from the material functions of polymer melts and solutions. Orbey and Dealy (1991) reported a comparison of such procedures.

In our case, the relaxation spectrum was calculated from experimental dynamic data using Pade'-Laplace (PL) procedure. PL method is one of the versatile tools for estimation of parameters of generalized Maxwell model from linear viscoelastic experiments. Fulchiron et al. (1993) showed, by using stress relaxation experiments, that the parameters of generalized Maxwell model can be extracted robustly and without a priori assumption about either the number of Maxwell modes, or initial guesses for their values. Simhambhatla and Leonov (1993) provided a more detailed description of PL method and extended its application for obtaining the Maxwell modes from dynamic data. They also demonstrated how the discrete relaxation spectrum found by PL procedure approximates a given continuous viscoelastic spectrum. Based on this work, Simhambhatla developed later a software, which worked well in our and other labs. This software was used in the present work.

In the case of highly filled polymer systems, PL method does not work at common low amplitudes of oscillations because the non-linear rheological response occurs for these systems even for small strains. The reason is the very strong particle-matrix or particle-particle interaction in the highly loaded filled systems, even for small deformations. No other specific technique exists that could discretize the thixotropic and viscoelastic spectrum. In such cases, the relaxation spectrum is obtained by solely fitting the data using nonlinear curve-fitting techniques.

It has already been proven that our dynamic data are really linear, i.e., they are independent of the amplitudes of oscillation in the range of 0.5% to 2.0%. From our dynamic data for polyamide-6/clay nanocomposite system, one can see that the plot of (G'') $G(\omega)$ loss modulus vs frequency is quite comparable with that for the neat polyamide-6 system, as non-terminal behavior for $G'(\omega)$ dominates. A hint of the plateau observed for $G'(\omega)$ in low frequency region (0.05–0.1 rad/s) indicates possible yield-like behavior in this system. This can be attributed to the direct interactions of platelets dispersed in the polymer matrix, along with strong interactions of the platelets with the PA6 matrix. If one extracts this yield value from the experimental data, the data could be viewed as representing a "neutral" suspension of plate-

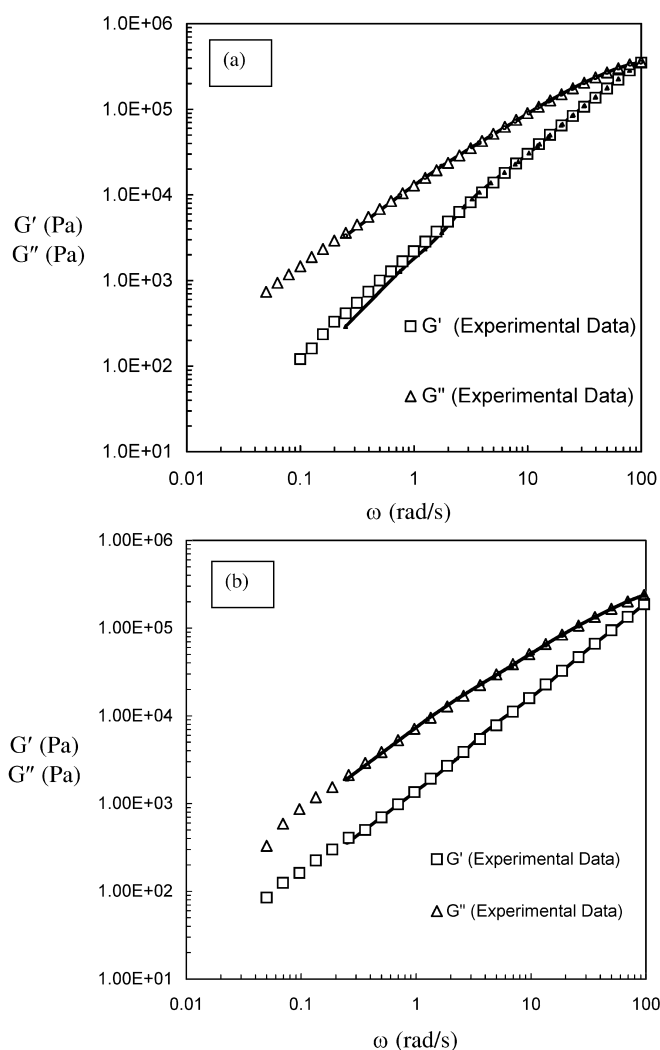


Fig. 8a,b Comparison of calculated and experimental storage and loss moduli of neat PA-6 and PA-6/clay nanocomposite. Data measured at: **a** 250 °C; **b** 260 °C

lets, non-interacting with each other and having interaction only with polymer matrix. Therefore the PL method would be appropriate for estimating the relaxation spectra for such a situation.

Table 2 Maxwell modes found from $G'(\omega)$ and $G''(\omega)$ data obtained for PA-6/clay nanocomposite at 250 °C and 260 °C

Temperature (°C)	Relaxation time (θ)(s)	Relaxation modulus (G)(Pa)
250	0.00765	6.00×10^5
	0.039	9.45×10^4
	0.29	1.50×10^4
260	0.0059	5.20×10^5
	0.037	5.66×10^4
	0.28	8.76×10^3

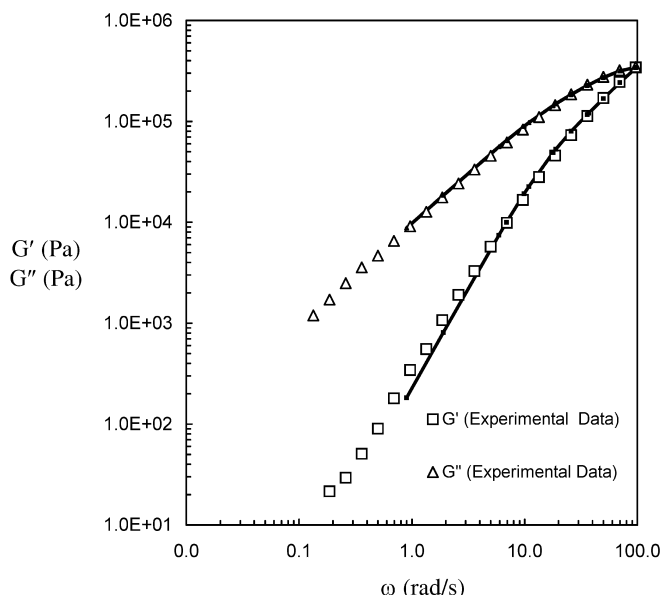


Fig. 9 A comparison of the measured (*symbols*) and simulated (*lines*) frequency dependencies of storage and loss moduli of neat PA-6 at small strain amplitudes. Data measured at 250 °C

As discussed before, the approximation of complex terminal behavior of filled polymers by a simple yield-like description is very rough. Since the real yield value could not be really observed, we treat the *apparent yield* value G_0 as an additional fitting parameter, reasonably choosing it from dynamic data. Because the PL procedure can determine the discrete relaxation spectrum using only the $G''(\omega)$ data, the curve $G'(\omega)$ was calculated with determined spectrum after that. It allowed us to find the best approximation for the apparent yield value G_0 from the $G'(\omega)$. The yield value G_0 estimated in such a way from the plot of $G'(\omega)$ was observed to be ~ 200 Pa at 250 °C, and ~ 100 Pa at 260 °C, thus illustrating its temperature dependence. The PL analysis combined with non-linear regression resulted in determining three relaxation modes for the nanocomposite system.

As shown in Fig. 8a,b, these modes describe fairly well the experimental plots $G'(\omega)$ and $G''(\omega)$. Figure 8c,d compares the experimental data and with calculated curves (using PL procedure) for dynamic moduli with

Table 3 Maxwell modes found from $G'(\omega)$ and $G''(\omega)$ data obtained for neat PA-6 at 250 °C and 260 °C

Temperature (°C)	Relaxation time (θ)(s)	Relaxation modulus (G)(Pa)
250	0.0082	6.5×10^5
	0.045	9.0×10^4
260	0.0075	6.5×10^5
	0.032	6.59×10^4

the Maxwell modes obtained at 260 °C for PA-6/clay nanocomposite. The tabulated relaxation spectra observed at the two temperatures 250 °C and 260 °C are shown in Table 2.

The comparison between behavior for the nanocomposite and neat polymer systems has already been demonstrated. To characterize completely the observed difference in the behavior of the two systems, we analyzed the dynamic data for neat polyamide-6 using PL method. Since the data observed are typical for viscoelastic liquids, we did not need to extract any yield value and refining the modes using non-linear regression. The comparison of experimental data and those presented by PL calculations for $G'(\omega)$ and $G''(\omega)$ using the relaxation spectrum obtained at 250 °C by PL method is shown in Fig. 9a,b, respectively. The Maxwell modes obtained at temperatures 250 °C and 260 °C using PL-analysis are tabulated in Table 3. Thus it is seen that only two found Maxwell modes describe well the oscillatory data for neat PA6 material.

We now compare the relaxation spectra, found from experimental data, with use of PL method at the two temperatures for the filled and unfilled polymer systems. The first two modes for the nanocomposite system and the two modes for the neat system are very close to each other at the respective temperatures. Therefore these relaxation modes could be attributed to the relaxation mechanisms in the polymer matrix. The third mode found for nanocomposite system that have a comparatively long relaxation time is not detected for neat polymer system. Hence we can attribute this relaxation mode to the structural influence of the clay platelets dispersed in the polymer matrix. It may be due to the flow of the platelets under shear, coupled with the internal rotations of the platelets. Thus the flow activation energy required for nanocomposites would be much more than that for the neat polymer system. These effects could be important for nanocomposite processing as well as for their post-processing applications.

Conclusions

In this paper we presented the results of rheological studies for a low loaded polymer/layered silicate nanocomposite as compared to the neat polymer system in the melt state. The apparent yield in nanocomposites has been qualitatively explained in terms of particulate network formation due to the strong polymer-filler and filler-filler interactions above the percolation threshold. The Pade'-Laplace analysis of the linear dynamic data for nanocomposite revealed the third, long time relaxation mode in the relaxation spectra, in addition to two other quite comparable Maxwell modes in both the polymer systems. Thus we attributed these two modes to the relaxation mechanisms of neat polymer matrix, while

the third mode presented in nanocomposite may be due to the structural effects of clay platelets dispersed in the polymer matrix.

Our study also throws light on many important aspects of rheological behavior of polyamide-6, one of the major engineering thermoplastics used worldwide. Because polyamide-6 strongly interacts with the clay platelets, it is one of the major polymers, sought for using as polymer matrix for preparing nanocomposites. Hence its separate rheological and mechanical features found in this paper are important. We also showed that studying the rheology of this material requires meticulous observations and analyses to present the

results without ambiguities such as thermal instability or insufficient melting of the polymer itself due to the presence of platelets. Thus not only the choice of the polymer matrix but also these related issues must be considered while analyzing the structure-property relationships in these novel materials. Additionally, the PL analysis employed in the paper could be used for explanation of the structural effects of the clay platelets.

Finally, this paper also presented new data for non-linear rheological behavior of nanocomposites. We hope that these data will be useful in further experimental and theoretical studies of these materials.

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