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Melt Compounding of Different Grades of Polystyrene With Organoclay. Part 2: Rheological Properties

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Polystyrene-based nanocomposites (PNC) were prepared using three grades of polystyrene (different molecular weights). The resin was melt-compounded with 0 to 10 wt% of commercial organoclay in a co-rotating twin-screw extruder. Owing to thermo-oxidative degradation the degree of dispersion was poor. The rheological properties of PNC were determined under dynamic and steady state shear as well as under extensional flow conditions. At the higher clay content, dynamic strain sweep demonstrated that the storage and loss moduli decrease continuously with an increase of strain. To characterize this nonlinear viscoelastic behavior, the Fourier-transform rheology was applied. The low strain frequency sweep showed that the storage and loss moduli increase with organoclay content. The extracted zero-shear viscosity data were used to calculate the intrinsic viscosity and then the aspect ratio of dispersions. In spite of nonlinear viscoelastic behavior, the time-temperature superposition was observed in the full range of concentration. The horizontal and vertical shift factors were found to be almost independent of organoclay content and molecular weight of PS. For comparison, PNC was also prepared by the solution method. A high degree of dispersion was obtained, reflected in the aspect ratio: $p = 269$, to be compared with $p = 16$ calculated for the melt-compounded PNC. *Polym. Eng. Sci.* 44:1061–1076, 2004. © 2004 Society of Plastics Engineers.

INTRODUCTION

General

The rheological properties of polymer nanocomposites (PNC) are pertinent to processing. The first use of an organoclay in polymers was to reinforce elastomers (1). The authors combined montmorillonite (MMT) pre-intercalated with diverse onium compounds, with elastomeric latex, and then processed the PNC by

standard methods. In 1961, Blumstein polymerized vinyl monomers (e.g., methylmethacrylate) in the presence of intercalated MMT (2). In 1963 Nahin and Backlund patented low-density polyethylene (LDPE)-organoclay 1:1 compositions (3). The patent also discussed compositions with polyvinylchloride (PVC) and polystyrene (PS).

In 1976, Fujiwara and Sakamoto (from Unitika) filed a patent application for the use of ammonium-salt intercalated clays during polymerization of polyamide (PA) (4). A few years later, Toyota obtained a U.S. patent for the polymerization of several vinyl monomers, e.g., styrene, in the presence of clay (5). However, since the composition contained 85 wt% of clay, exfoliation was

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impossible. Nevertheless, enhanced mechanical performance was reported. In the following years, attention shifted to the opposite end of the concentration range—to the dispersion of small quantities of clay in PA-6 (6–8). The authors prepared these PNC by dispersing montmorillonite (MMT) pre-intercalated with ω -amino lauric acid in ϵ -caprolactam, followed by polymerization. Since the intercalant participated in the ring-opening polymerization, a virtually ideal PNC was obtained—exfoliated and with matrix end-tethered to clay platelets. Flow and processability of the new material were excellent.

AlliedSignal elected to use melt exfoliation (9–11). The process involved the use of organo-silanes, organo-titanates or organo-zirconates that facilitated clay dispersion and improved the thermal stability at temperatures above 300°C. More details can be found in a recent monograph (12).

Systematic rheological studies on PNC are more recent. A relatively early publication reported on the steady-shear flow of MMT, pre-intercalated with dimethyl di-tallow ammonium, dispersed in either diphenyl dimethyl siloxane or in polydimethylsiloxane (PDMS) (13). In the former system, clay was intercalated, whereas in the latter it was exfoliated. Characteristically, the flow curves showed large Newtonian plateaus, indicating absence of a 3D structure—in other words, the interaction between organoclay particles was weak. As expected, the zero-shear viscosity, η_0 , increased with organoclay loading, but at high rates of deformation, the matrix viscosity was almost recovered. The plot of relative viscosity, η_r , vs. ϕ indicated that, while for the exfoliated system (up to 13 wt%) the dependence is typical for diluted (i.e., non-interacting) suspension with high value of the intrinsic viscosity: $[\eta] = 9.3$, the intercalated system gave evidence that interactions between nearly spherical stacks of clay platelets start at low loading of ca. 4 wt%. The nanoparticles, exfoliated or not, behaved as solid fillers.

Krishnamoorti and Giannelis (14) studied flow of poly- ϵ -caprolactone/MMT (PCL/MMT) and PA-6/MMT, prepared by polymerization in the presence of clay pre-intercalated with ω -amino lauric acid. The process ensured direct bonding between MMT surface and macromolecules—a hairy clay platelet (HCP) structure. The authors labeled these systems as “end-tethered.” For PCL/MMT, the validity of the time-temperature (t - T) superposition was reported. The Arrhenius plot of the frequency shift factor, a_T vs. $1/T$, did not depend on the clay loading. Thus, excepting the apparent yield behavior at low frequencies, the matrix polymer dominated the flow. The PA-6/MMT nanocomposites contained 0, 2 and 5 wt% organoclay. The G' and G'' moduli increased with clay loading. Their power-law dependence in the terminal zone ($\omega < 10$ rad/s) changed with organoclay concentration. Thus, for 0, 2 and 5 wt% loading the initial slope: $g'' = (d \log G''/d \log \omega)_{\omega < 10} = 0.93, 0.80$ and 0.70 , respectively. These values should be compared to expectations, viz. $g'' = 1$ for neat polymer, $g'' = 0.5$ for the liquid crystal polymer (LCP) domain flow, and $g'' = 0$

for systems with the yield stress. Thus, these PNC behaved like solutions of LCP rather than as a filled melt with yield stress.

Sometimes, end-tethering may be replaced by strong interactions between polar groups and clay surface. Schmidt *et al.* (15) measured birefringence and small angle neutron scattering (SANS) during Couette flow of clay suspensions in aqueous polymer solution. Thus, synthetic hectorite was dispersed in aqueous solution of polyethylene glycol (PEG, $M_w = 10^3$ kg/mol). The birefringence indicated mechanical coupling between clay platelets and PEG. At low rates of shear, $\dot{\gamma} < \dot{\gamma}_{critical} \cong 30$ (s⁻¹), birefringence was dominated by clay platelets, but at high shear rates, it was dominated by the polymer chains stretched in the flow direction. SANS data indicated that at $\dot{\gamma} > \dot{\gamma}_{critical}$ the flow is strong enough to induce chain orientation. The clay platelets (within aggregates with diameter $d = 32 - 233$ nm) were oriented in the flow direction with the surface normal in the neutral (not radial) direction.

Similar results have been obtained for nanocomposites with other polymers as a matrix, viz. PCL (16), polypropylene (PP) (17, 18), PA-12 (19), PEG (20), poly(styrene-*b*-isoprene) PS-PI block copolymer (21, 22), PS (23–25), etc. The values of the initial slope, g' or g'' , depend on the degree of dispersion and concentration of organoclay platelets. Thus, at low frequency, the viscosity of nanocomposites is larger than that of neat polymers, but at high deformation rates the data for PNC are frequently comparable to these obtained for neat polymeric matrix. Furthermore, because the clay platelets align during flow, the power-law index for PNC is smaller after shearing than before (24). When the clay content increases, the transition from the Newtonian to the power-law flow region shifts toward lower frequency (17, 20, 28). Especially, at high clay loadings (e.g., $w \geq 10$ wt%), the Newtonian plateau disappears for frequencies $\omega \geq 0.1$ rad/s. However, for dilute, linear viscoelastic systems, the relative viscosity of PNC follows the standard η_r vs. ϕ dependence.

The extensional flow of PNC has been studied by Okamoto *et al.* (26) The authors investigated the effects of elongational flow on clay platelet alignment in PP-based nanocomposites. Strong strain hardening (SH) and rheopectic behavior were found to originate from perpendicular alignment of the clay platelets to the stretching direction. Kotsilkova (27) also reported SH for reactively exfoliated PNC of polymethylmethacrylate (PMMA) with MMT.

Recently, a study on the dynamic flow behavior of PA-6 and its PNC with 2 wt% of organoclay was published by Utracki and Lyngaae-Jørgensen (28). The two materials were extruder-blended in proportions of 0, 25, 50, 75 and 100 wt% PNC. The dynamic shear rheological properties of well-dried specimens were measured under N₂ at $T = 240^\circ\text{C}$. At constant T , ω and strain (γ) the time sweeps resulted in significant increases of the shear moduli. The γ and ω scans showed a complex rheological behavior of all clay-containing specimens. At $\gamma = 40\%$ linear viscoelasticity was observed only for

0 and 25 wt% of PNC. For compositions containing > 25 wt% PNC, two types of nonlinearity were detected. At $\omega \leq \omega_c = 1.4 \pm 0.2$ rad/s an apparent yield stress provided evidence of a 3D structure. At $\omega > \omega_c$, G' and G'' were sensitive to shear history—the effect was reversible. From the frequency scans at $\omega > \omega_c$ the zero-shear relative viscosity vs. concentration plot was constructed. The initial slope gave $[\eta]$ from which the aspect ratio of organoclay particles, $p = 287 \pm 9$ was calculated, in agreement with the value calculated from the permeability data, $p = 286$. The behavior of these PNC was quite similar to that of liquid crystal polymers.

PNC with PS or its copolymer as a base have been prepared by polymerization (in solution, suspension or bulk) or by the melt-processing methods. In spite of extensive work, these systems did not reach commercialization. At the same time, because of the amorphous matrix, they offer great advantages as a model system for studies on, e.g., the mechanical or barrier properties. However, as will be evident from the few cases discussed below, exfoliation of clay in a PS matrix is difficult and requires careful consideration of the chemistry.

Flow of PS Nanocomposites

For most rheological studies the PNC specimens were prepared by polymerizing monomer(s) in the presence of organoclay, less frequently by the melt compounding in a laboratory-type mixer, viz. internal mixer or a kneader. The reactive route may be designed to lead to end-tethering, where the macromolecules are chemically bonded to the clay surface creating the “hairy clay platelets” (HCP). For example, Fu and Qutubuddin (29) prepared end-tethered PNC with PS matrix by pre-intercalating MMT with vinyl-benzyl-dimethyl dodecyl ammonium chloride (VDAC), dispersing it in styrene and copolymerizing. XRD and TEM of the samples indicated full exfoliation. Unfortunately, very limited information on rheology and mechanical behavior was provided.

Hoffmann *et al.* (23) prepared two types of CPNC by intercalating synthetic fluoromica with either amine-terminated PS (ATPS; $M_n = 5.8$ kg/mol) or 2-phenylethyl amine (PEA; $M_n = 121$ g/mol). The organoclays were compounded with the PS at 200°C for 5 min. According to XRD and TEM the PEA-system was intercalated $d_{001} = 1.4$ nm, while that with ATPS was exfoliated. The dynamic rheological measurements showed sharply different behavior of these two systems. The presence of 5 wt% clay in PEA-system caused $G' = G''(\omega)$ to parallel the dependence of the matrix with only slightly higher values caused by the filler effect. In the exfoliated ATPS-system, the low-frequency slope in the terminal zone was about $g' = 0.5$ (instead of 2, as in the former case). The authors concluded that in the presence of ATPS, the clay platelets formed a network. They ascribed the large difference in behavior to the length of the intercalating compound—one may control the degree of intercalation/exfoliation by varying the chain length of the intercalant.

A more recent publication from the same laboratory extended this work to a series of compositions containing 0 to 10 wt% of organoclay (30). Good t - T superposition was obtained, with WLF c_1 and c_2 constants virtually identical to those for the PS matrix. The analysis of the dynamic data showed a dramatic change in the van Gurp plot of $\arctan G''/G'$ vs. complex modulus, G^* —the dependencies for PS and for PS with PEA-system were virtually identical, but quite different from that of ATPS-systems. Furthermore, it was observed that the plateau moduli follow the dependence: $G_N^0 \propto 1/\phi_{PS}^n$, where ϕ_{PS} is PS matrix volume fraction, and the exponent $n = 0$ for PEA-system, and $n = 2$ for ATPS-systems. These findings confirm the theoretical conclusions by Balazs and her colleagues (31, 32).

However, there is also evidence that modification of the flow behavior (in comparison to the classical filled systems) is possible without end-tethering. One of the examples comes from Ren *et al.* (21). The authors dispersed ≤ 9.5 -wt% organoclay (MMT intercalated with a di-methyl di-octadecyl ammonium) in a toluene solution of polystyrene-*b*-polyisoprene (PS-PI). A moderate intercalation was obtained with the interlayer spacing $d_{001} = 2.1$ to 2.5 nm, independent of the clay content. Linear viscoelastic flow was studied at $T = 80^\circ\text{C}$ – 105°C . The t - T superposition required simultaneous vertical and horizontal shifting of the shear moduli to produce master curves: $b_T G'$ or $b_T G''$ vs. $a_T \omega$. While the plot of a_T vs. T was common for all compositions, b_T did not—the neat copolymer data followed different dependence than those for the PNC. The stress relaxation in the terminal zone indicated solid-like behavior. The effect was pronounced at ≥ 6.7 wt% organoclay, resembling that observed for the exfoliated end-tethered nanocomposites where $g' = (d \log G'/d \log \omega) \cong 0$. Considering the small degree of interlayer expansion, the strong concentration dependence of G' and G'' is unexpected. The authors attributed this behavior to stacks of intercalated clay platelets forming a 3D network. However, during the solution blending of the organoclay with PS-PI, it was the PS block that diffused into the interlamellar galleries, which suggests some miscibility between organoclay and PS. Thus, in the two-phase copolymer matrix, clay is preferentially located in the PS-block phase. Formation of the 3D structures is probably due to the interaction between the domains reinforced by MMT PS and enrobed in PI. This situation resembles well-compatible immiscible polymer blends. Ren *et al.* (21) also showed that the simple relation developed by Ferry (33) for single component melts is also valid in these rheologically complex systems:

$$G(t) \Big|_{t=1/\omega} = G'(\omega) - 0.4 G''(0.4 \omega) + 0.014 G''(10 \omega) \quad (1)$$

Lim and Park (24, 25) prepared PNC by melt compounding in an internal mixer Cloisite® 6A with either PS or in PS-co-MA, expanding the interlayer spacing by $\Delta d_{001} = 0.51$ and 0.43 nm, respectively. In spite of similarity in d_{001} , the low frequency dynamic moduli showed

large differences between the two PNC, viz. G' ($\omega = 0.02$) $\cong 0.1$ and 6 kPa, with the corresponding differences in the initial slope of $g' = 0.59$ and 0.24, respectively. The ratio G' (CPNC)/ G' (matrix) dramatically decreased with frequency, eventually becoming unity. This effect was much sooner achieved for PNC with PS as the matrix than with PS-co-MA. Shearing the latter system at $\gamma = 120\%$, $\omega = 1$ rad/s for 30 min reduced the association, but did not eliminate them entirely. In short, the presence of -MAH groups significantly increased the tendency of intercalated clay stacks to form 3D structures.

The cited examples demonstrate that instead of a sharp distinction between the classical composites and the PNC, the influence of organoclays shows a continuous spectrum of rheological behaviors. The LCP-type of flow observed for PA-6 nanocomposites originates from HCP. Calculations indicate that there are over 1000 macromolecules attached to an average clay platelet. These highly branched entities easily entangle, engendering what has been considered a typical rheological response of PNC. However, as the above examples illustrate, there are other mechanisms responsible for generating 3D structures.

In aqueous media the electrostatic interactions force the platelets to form the edge-face "house-of-cards" structures, even at low loadings (system gels above 5 wt% clay!). In organic media the formation of 3D structures is possible by two mechanisms—crowding of solid particles (as in classical composites), or by entanglements. The former mechanism requires two elements: concentration that exceeds the "maximum packing volume fraction, ϕ_m ," and nonrepulsive interaction between the particles. In the latter case the strongest effects are to be expected for the HCP, when the terminal groups directly bond macromolecules to the clay surface. However, entanglements may also be promoted by the use of block copolymers or by forming associations between clay surface and polar groups of the polymer chain. Further examples of the effects of tethering will be found in the following parts.

Okamoto *et al.* (34) intercalated Na-MMT either with oligo(oxy-propylene) diethyl methyl-ammonium chloride, or methyl-trioctyl-ammonium chloride (SPN or STN, respectively). Polymerization of methylmethacrylate or styrene in which the organoclays were dispersed resulted in fully exfoliated PNC of SPN in PMMA and intercalated PNC of STN in PMMA and of SPN in PS. The frequency sweeps detected two types of rheological behavior: the intercalated systems showed solid 3D, gel-like behavior with frequency-independent initial slope, $g' = g'' = 0$. By contrast, the exfoliated PNC reduced the inter-domain interactions.

Kim *et al.* (35) emulsion polymerized PS in the presence of highly swollen Na-MMT. Polymerization slightly increased d_{001} . Thus, it resulted in poor dispersion in the PS matrix. The flow curves, $\log \eta$ vs. $\log \dot{\gamma}$, followed the simple Carreau dependence for monodispersed systems:

$$\eta = \eta_0 / [1 + (\tau^* \dot{\gamma})^{1-n}] \quad (2)$$

Here, η_0 is the zero shear rate viscosity, τ^* is the longest relaxation time, and n is a power-law exponent. From the listed values of η_0 the intrinsic viscosity, $[\eta] = 112$, and then the aspect ratio $p = 270$ were calculated. Thus, the assemblies of intercalated MMT platelets are highly anisometric. In consequence, scans performed first increasing and then decreasing the rate of shear resulted in a hysteresis loop, with the former data forming the upper branch. The size of the loop increased with clay concentration.

In conclusion, a variety of PNC have been prepared with PS as the matrix, from the end tethered, fully exfoliated to nontethered but exfoliated, to intercalated and finally to suspensions of clay stacks. The rheological studies on these systems are infrequent and fragmentary. These different structures result in different rheological responses, but the effect of structure on flow is not always easy to predict.

The main objective of this study is to examine diverse rheological methods for the characterization of polymeric nanocomposites, PNC. For this purpose a variety of rheological tests have been carried out, including dynamic and steady state shear flow in the linear and nonlinear viscoelastic modes of deformation. Similarly, extensional flow was conducted in two rheometers, observing linear deformability as well as strain hardening. The usefulness of the rheology for determination of the degree of dispersion, for characterization of 3D structure as well as presence or absence of the thermodynamic miscibility will be discussed.

EXPERIMENTAL

Materials and PNC Preparation

Nova Chemicals provided the three grades of commercial PS. Their weight average molecular weights (M_w) and melt flow rates (MFR) are listed in Table 1. The characteristics of organoclay, Cloisite® 10A (C10A; purchased from Southern Clay Products), are also given. Three series of PS/organoclay mixtures were prepared using the Leistritz co-rotating twin-screw extruder TSE-34 ($L/D = 40$). Compounding was carried out at barrel temperature of 200°C, screw speed of 200 rpm, and PS feed rate of 5 kg/h. Organoclay was added to molten polymer from a side feeder. Table 2 shows the polymer and organoclay feed rates, the calculated and the actual (determined by TGA) organoclay content.

The great majority of work discussed in this paper was carried out on melt-compounded samples. However, for comparison one sample was prepared by the solution intercalation method. First, 1 wt% of C10A was dispersed in toluene for 30 min, then ultrasonicated for 1 h (10 MHz, 600 W) at room temperature, and then stirred at 60°C for 24 h. The clay suspension was slowly introduced into solution containing 5 wt% PS1301 in toluene and then stirred for 8 h at room temperature, and then seven days at 70°C. Next, the PNC was precipitated with methanol, filtered, washed with excess MeOH and then dried under dynamic vacuum for 6 weeks, at increasing temperature (from 60°C to 80°C).

Table 1. Material Characteristics.

Material	Supplier	Specification
PS 1220	NOVA Chemicals	$M_w^1 = 310$ kg/mol; MFR ² = 1.9 g/10 min
PS 1301	NOVA Chemicals	$M_w^1 = 270$ kg/mol; MFR ² = 3.5 g/10 min
PS 1510	NOVA Chemicals	$M_w^1 = 230$ kg/mol; MFR ² = 6.5 g/10 min
Organoclay (Cloisite® 10A)	Southern Clay Products (SCP)	Na-MMT ³ intercalated with 2MBHT: Organic loading = 1.25 meq/g Organic content = 39 wt% Interlayer spacing: $d_{001} = 1.92$ nm

Notes: ¹Measured by Nova Chem.;²by ASTM D1238, Procedure B; 200/5.0;³SCP: CEC = 0.926 meq/g; $d_{001} = 1.17$ nm; 2MBHTA = di-methyl, benzyl, hydrogenated tallow ammonium chloride (tallow contains: ~65% C₁₈; ~30% C₁₆; ~5% C₁₄).Table 2. Feed Rates From Hopper $Q_h = 5$ kg/h and From Side Feeder, Q_{sf} (kg/h), and Resulting Organoclay Concentration, w (wt%).

PS	Q_{sf} (kg/h)	Calculated ¹ w_c (wt%)	Measured ² w_m (wt%)	ΔQ_{sf} (%) ³
1220	0	0	0	0
	0.05	1.0	1.3	30
	0.1	2.0	2.5	25
	0.25	4.8	5.6	17
	0.5	9.1	11.1	22
1301	0	0	0	0
	0.05	1.0	1.4	40
	0.1	2.0	2.8	40
	0.25	4.8	5.7	19
	0.5	9.1	10.6	16
1510	0	0	0	0
	0.05	1.0	1.5	50
	0.1	2.0	2.1	5
	0.25	4.8	6.0	25
	0.5	9.1	10.6	16

Notes: Compounding conditions: barrel temperature 200°C, screw rotation speed 200 rpm;

¹Calculated from the feed rate from hopper and side feeder;²Inorganic content determined by TGA, then the organoclay concentration calculated assuming that organic content in Cloisite 10A is 39 wt%;³The side feeder error was calculated as $\Delta Q_{sf} (\%) = 100 (w_m - w_c)/w_c$.

Dynamic Flow Tests

The dynamic rheological measurements were performed in an ARES rotational rheometer, using 25-mm-diameter parallel plates in oscillatory shear mode under a blanket of dry nitrogen at $T = 200^\circ\text{C}$. Prior to testing, the specimens were dried for at least 48 h under vacuum at 80°C . Three types of tests were carried out: 1) the time sweep at frequency $\omega = 6.28$ rad/s, and strain $\gamma = 14.7\%$ for time $t \leq 1083$ s; 2) the strain sweep at $\omega = 6.28$ rad/s, for $\gamma = 0$ to 100% at a rate of 2%/step; 3) the frequency sweep at $\gamma = 1$ and 40% within the frequency range from $\omega = 0.1$ to 100 rad/s. To test for the time-temperature superposition, G' and G'' were recorded at $T = 160^\circ\text{C}$, 200°C and 240°C . To examine the nonlinear viscoelastic behavior, the Fourier-transform rheology was carried out at $\omega = 6.28$ rad/s, $T = 200^\circ\text{C}$ and $\gamma = 10\%$, 20%, 50% and 75%. To observe the time-effects on the PNC structure the experiments were conducted for about 1 h taking the FTR spectra every 4–5 min.

Steady Shear Flow

Steady state shearing was carried out in an Instron capillary rheometer with a barrel diameter of 9.525 mm at 180°C . Four capillaries with diameter of 0.762 mm and the length-to-diameter ratios: $L/D = 5, 10, 20$ and 40 were used. The extrusion speed varied from 0.05 to 5 cm/min. The standard Bagley and Rabinowitsch corrections were applied.

Extensional Flow

Two elongational rheometers from Rheometrics were used, the Mündstedt-type (RER) and the Meissner-type (RME). The experiments were performed at 200°C . In both instruments the Hencky range of rates of deformation was $\dot{\epsilon} = 0.1$ to 1 s^{-1} . Owing to a mismatch of

density between the silicon oil bath and the immersed molten PS specimens, the deformation in RER was not uniform (sagging). The transducer signal from RME was corrected for material slippage between the rotating clamps. The maximum strain achieved in RER and RME was, respectively, $\epsilon \approx 3.0$ and 4.4. For reference, the stress growth function in shear was also determined.

RESULTS

Time Sweep

To develop the most appropriate test procedure three samples of neat PS1301 were tested: (a) as received, tested in air; (b) as received, tested in nitrogen (N_2), and (c) dried for at least 48 hrs at 80°C under dynamic vacuum and then tested under N_2 .

Figure 1 displays changes in the storage and loss moduli of PS1301 at 200°C . The data can be fitted to a third order polynomial:

$$G = \sum_{i=0}^3 a_i t^i; \quad dG/dt = \sum_{i=1}^3 i a_i t^{i-1} \quad (3)$$

where G is either G' or G'' and a_i are parameters. Differentiation leads to the rate of change, dG/dt , which subsequently may be used to correct the rheological data. The equation parameters are listed in Table 3.

As the data in Fig. 1 show, the “as received” not dry specimens show opposite tendency when tested in air or under blanket of dry N_2 . When testing in air, the specimen progressively oxidizes and the shear moduli decrease. By contrast, testing under N_2 result in an initial increase of moduli (by about 4%) and then stable response for at least 1 h. Since the specimens dried under vacuum did not show the initial increase, a slow evaporation of volatiles is the likely cause.

Fig. 1. Time sweep for PS1301 at $T = 200^\circ\text{C}$, $\omega = 6.28 \text{ rad/s}$ and $\gamma = 10\%$. Two "as received" samples tested: #1 not dried and tested under dry N_2 ; and #2 not dried and tested in air. The vertical double arrow indicates the experimental error of $\pm 2.5\%$.

All the subsequent rheological tests were conducted under dry N_2 after predrying the specimens under vacuum at 80°C for at least 24 h. The data were used directly, without correcting for the time-effects.

Strain Sweep

Figure 2 displays the storage and loss moduli (G' and G'' , respectively) as a function of shear strain at constant frequency ($\omega = 6.28 \text{ rad/s}$), for the three PS matrix resins and their PNC containing the nominal concentration of 10 wt% organoclay. For neat PS, the moduli are constant up to critical strain value, γ_c , and then decrease. The value of γ_c slightly decreases with PS molecular weight, viz. $\gamma_c \approx 36, 28$ and 24% for PS1510, PS1301 and PS1220, respectively.

For the PNC specimens, both shear moduli, G' and G'' , decrease within the whole strain range: (a) at low strains (e.g., $\gamma \leq \gamma_c$) the effect is related to the presence of organoclay, while (b) at high strains $\gamma > \gamma_c$ the decrease follows that of the matrix. At the highest strains (e.g., $\gamma > 80\%$) the readings are not reliable because of the sample loss from the tooling. Noteworthy, the loss was greater for the neat PS specimens than for the PNC.

Fig. 2. Storage and loss moduli at $T = 200^\circ\text{C}$ and $\omega = 6.28 \text{ rad/s}$ vs. strain for the three PS matrices and their PNC containing 10 wt% Cloisite® 10A.

Frequency Sweep and Steady State Shear Viscosity

Figure 3 shows the reduced plot of the shear moduli, $b_T G'$ and $b_T G''$, as a function of reduced frequency, $a_T \omega$, for the three PS resins and their mixtures with 10 wt% organoclay. Each curve was obtained by horizontal (by

Table 3. Polynomial Fit Parameters for the Time Sweep of PS1301: #1 Specimen Dried and Tested Under N_2 and #2 Not Dried, Tested in Air.

Sample PS1301	G' (kPa)				G'' (kPa)			
	a_0	$a_1 10^3$	$a_2 10^7$	$a_3 10^{11}$	a_0	$a_1 10^3$	$a_2 10^7$	$a_3 10^{11}$
#1: not dry, N_2	18.657	1.453	-6.380	9.053	20.594	1.149	-4.925	6.821
#2: not dry, in air	15.076	-0.930	2.973	-6.013	18.996	-1.011	2.975	-6.110
#3 dry, N_2	22.819	0.127	-0.663	0.978	23.107	0.0998	-0.630	0.966

Fig. 3. Frequency sweeps at 160°C, 200°C and 240°C after vertical and horizontal shift onto $T_0 = 200^\circ\text{C}$ master curve. Strain of $\gamma = 30\%$ was used. See text.

a_T) and vertical (by b_T) shifting of the data obtained at 160°C and 240°C onto those obtained at 200°C. At 30% strain, the shear moduli, G' and G'' , of PS with 10 wt% organoclay are only slightly larger than those of neat PS. Furthermore, the relative enhancement of moduli by incorporation of organoclay is almost independent of molecular weight of PS.

Another way of looking at G' and G'' is to treat them as coefficients of frequency, viz. the storage modulus coefficient ψ (a measure of elasticity), and the dynamic viscosity η' :

$$\psi = G'/\omega^2; \quad \eta' = G''/\omega \quad (4)$$

Figure 4 shows the frequency dependence of ψ and η' for PS and their PNC nominally containing 10 wt% organoclay. In the region of low frequency ($\omega < 0.1$ rad/s), both functions increase with molecular weight of PS and organoclay content. In the high-frequency region, ψ and

Fig. 4. Reduced frequency dependence at 200°C and $\gamma = 30\%$ of the storage modulus coefficient and dynamic viscosity. In the latter Figure the steady state viscosity for PS1301 and its PNC are also shown.

η' functions collapse into a single dependence, each. It is noteworthy that the steady state viscosity, determined in the capillary rheometer at $T = 180^\circ\text{C}$ and then shifted by a_T to 200°C, $\eta = \eta(a_T \dot{\gamma})$, follows the dependence of $\eta' = \eta'(a_T \omega)$.

Fourier-Transform Rheology (FTR)

Application of the Fourier transform methodology to rheological problems (FTR) is several decades old (36, 37), but it gained prominence more recently as a tool for the analysis of nonlinear viscoelastic response in polymeric systems subjected to large amplitude oscillatory shear (38).

FTR was applied to analyze the nonlinear viscoelastic behavior of the PNC series with the most viscous matrix, namely with PS1220. Example of data observed in the Fourier space is displayed in Fig. 5. Similar responses were observed for other compositions, including PS1220.

Extensional Flow

Three types of measurements were carried out:

1. Shear stress growth function at 200°C and low rates of shearing, $\dot{\gamma} = 0.002 \text{ s}^{-1}$. The shearing was carried out for 1000 s, between 25-mm-diameter parallel plates with gaps of 1.2 to 1.5 mm. Since compression molding was found to significantly reduce PNC melt viscosity, dried pellets from the compounding extruder were used for the tests.
2. Extensional stress growth function in Rheometrics Extensional Rheometer (RER, or Mnstedt-type device (39)) at constant Hencky strain rate mode: $\dot{\epsilon} = 0.1$ to 1.0 s^{-1} . The tests were carried out at 200°C in Dow 200 silicone oil. The specimens were molded into 22 mm long cylinders, with diameter of $5.55 \pm 0.05 \text{ mm}$. The procedure is described elsewhere (40).
3. Extensional stress growth function in Rheometric Scientific RME, a commercial version of the Meissner device (41). The tests were carried out at 200°C, at constant Hencky strain rates: $\dot{\epsilon} = 0.1$ to 1.0 s^{-1} . The specimens were molded into slabs with approximate dimensions of $60 \times 7 \times 1.8 \text{ mm}$.

The instrument requires correction of data by means of independent strain measurements (42). Accordingly, the deformation was video-recorded and the corrected strain rates were used to recalculate the stress growth function. Results are shown in Fig. 6.

The RER stress growth function followed the stress growth function in shear, viz. $\log \eta_E^+(t) \cong \log [3\eta_s^+(t)]$, thus no strain hardening (SH) was observed. By contrast, the corrected RME data showed SH at all deformation rates, for all specimens (viz. Fig. 7), including PS1220. Three mechanisms may explain the difference: difference in platelets orientation in the transfer moldings for RER than that in compression molded bars for RME, diffusion of silicone oil into PS matrix and non-uniform deformation of specimen (sagging).

DISCUSSION

General Thermal Effects

Characteristics of the material discussed in this paper were described elsewhere (43). Thus, XRD showed two peaks, located at 2θ of about 2° and 5.5° . The former indicated that owing to diffusion of PS macromolecules, the organoclay interlayer spacing expanded from $d_{001} = 1.93$ to 4.20 nm , while the latter indicate the reduction of interlayer spacing of organoclay during the compounding to 1.6 nm . The TEM qualitatively agreed with the XRD data; low magnifications showed the presence of large clay aggregates, whereas high magnification

Fig. 5. FTR diagrams for PS1220 with 10 wt% Cloisite® 10A as a function of frequency and strain at $T = 200^\circ\text{C}$. The input frequency was 6.28 rad/s .

Fig. 6. RME Hencky strain rate calibration for PS1220 and its PNC containing 2 and 10 nominal wt% of organoclay. Solid symbols represent results for lower (L) and upper (U) rotating clamps; open symbols those for only L clamps.

showed individual clay platelets and short, expanded stacks. The FT-IR results provided evidence for the thermo-oxidative degradation of the onium compound, leading to breakdown into benzyl dimethyl amine and a long-chain olefin able to react with oxygen. The formed peroxides in turn may cause chain scission of PS macromolecules.

It is known that in the absence of oxygen, the principal thermal degradation mechanism of PS is the chain depolymerization ("unzipping") that starts at $T > 300^\circ\text{C}$, and it produces volatiles (no char) containing ca. 50% of styrene. However, in the presence of oxygen, PS degrades at lower temperatures by mechano-chemical processes. As Fig. 1 demonstrates, there is significant difference in rheological response whether "as received" (neither dried nor extruded) PS is tested in air or under N_2 . In air, even under relatively mild stress, the moduli decrease by ca. 15% in 1 h. By contrast, under a blanket of dry N_2 the samples are relatively stable. Owing to evaporation of volatiles, the moduli in one hour increase by about 4.5%. The data are well described by third-order polynomial with the parameters listed in Table 3. At the end of the devolatilization ($t \approx 2000$ s), the rate of G' and G'' change, is respectively: $dG'/dt = -0.013$ and 0.002 (Pa/s) for the sample tested under N_2 ; and specimen $dG'/dt = -0.462$ and -0.554 (Pa/s) for tested in air. In short, testing dried specimens under N_2 generates stable, reproducible data with experimental error of about $\pm 2.5\%$, eliminating any need for numerical corrections.

Effect of Clay Dispersion on Rheology

Presence of solid particles increase the energy loss during flow, which in simple form is given by the Einstein relation for the relative viscosity of hard sphere suspensions:

Fig. 7. Stress growth functions at $T = 200^\circ\text{C}$ in shear (solid line) and in elongation for PS1220 containing 2 wt% organoclay.

$$\eta_r \equiv \eta/\eta_0 = 1 + [\eta]\phi + O(\phi^2) \dots \quad (5)$$

where $[\eta]$ is the intrinsic viscosity—a measure of the hydrodynamic volume of dispersed particles, and ϕ is the volume fraction of dispersed solid. According to Einstein, $[\eta] = 2.5$ for monodispersed, nonadsorbing hard spheres. As the degree of particle symmetry decreases, i.e., as its aspect ratio, p , increases so does $[\eta]$. Several theoretical and empirical relations between these two quantities are available (12). For disks the following dependence was found:

$$[\eta] = 2.5 + a(p^b - 1); \quad a = 0.025 \pm 0.004; \quad b = 1.47 \pm 0.03 \quad (6)$$

As a first approximation, the preparation of PNC can be regarded as a dispersion of clay platelets in molten polymer, thus as a progressive change of the aspect ratio from $p \approx 1$ to about 300 (a common value for commercial organoclays). According to the above relations, dispersion of 2 wt% organoclay should change η_r from 1.02 to 1.8. This large effect is further augmented by at least three secondary influences: 1) adsorption of organic molecules on the high energy solid surface, and associated with it loss of free volume and chain mobility (44); 2) chemical bonding of clay platelets to the matrix, e.g., by end-tethering (8); and 3) formation of 3D structures by physical (geometric) or chemical (entanglements) interactions (28). In short, rheological measurements at low deformation rates (to prevent destruction of structures) provide potentially the most sensitive method for the characterization of nanocomposites. They are also more informative for processing, than the most commonly used XRD and TEM. The rheological response of PNC with well-dispersed, exfoliated, clay platelets depends on strain, stress and time. The effect is particularly large at low frequency—the moduli, G' and G'' , are

greatly increased above the values of neat polymer (25, 28). The ability of clay platelets to interact depends on the degree of dispersion, aspect ratio, concentration and orientation. In the following text, several rheological methods for detecting the degree of clay dispersion will be examined. The data for the poorly dispersed melt-compounded PNC will be compared with chemically identical, but solution-dispersed one.

Dynamic Flow

Three types of dynamic tests were conducted: time, strain and frequency sweeps. The time sweeps at strain of $\gamma \cong 30$ (%) and frequency of $\omega = 6.28$ (rad/s) produced a stable signal, insensitive to clay content up to 10 wt%. In the melt-compounded PS nanocomposites, the partial decomposition of ammonium intercalant resulted in poor dispersion. Furthermore, there is no covalent bonding between clay and the matrix. As a result, the interactions are weak and, at $\gamma = 30\%$ the fragile structure is nearly destroyed (see Fig. 2).

The strain sweeps at $\omega = 6.28$ (rad/s) provide more information. To quantify effects of the clay content on the relative shear moduli at $T = 200^\circ\text{C}$ the ratio: $G_R = G(\text{PNC})/G(\text{PS})$ at the lowest reliable strain, $\gamma = 3\%$ are plotted in Fig. 8 as a function of organoclay content. The increase is modest, significantly smaller than that observed for the exfoliated PA-6 based nanocomposites (28). The dependence may be approximated by Einstein's Eq 5 with $[\eta] \leq 4$; hence $p \leq 15$. Thus, under the low strain dynamic tests at $\omega = 6.28$ rad/s the dynamic flow is dominated by stacks of clay platelets with low aspect ratio. Assuming a diameter of a clay platelet of 300 nm, the stack height would be larger than 20 nm; hence containing at least 10 clay platelets. As Fig. 8 shows, the concentration effect, thus dispersion, is nearly independent of the matrix.

Fig. 8. The effect of organoclay content on the relative modulus for the three series of PS-based PNCs. For clarity, the values for loss modulus are shifted up by 0.1. The hard-sphere dependence is shown as a straight chain line.

By application of the time-temperature (t - T) superposition principle, the frequency sweep at strain of $\gamma \cong 30$ (%) was extended over six decades of frequency. It is evident from Fig. 3 that only the low-frequency region, $\omega a_T < 1$ (rad/s), reflects the PNC interactions. At these low frequencies simple proportionalities are observed:

$$\begin{aligned} \log G' &\propto g' \log \omega; & g' &\equiv (\partial \ln G' / \partial \ln \omega)_{\gamma, T, P} \\ \log G'' &\propto g'' \log \omega; & g'' &\equiv (\partial \ln G'' / \partial \ln \omega)_{\gamma, T, P} \end{aligned} \quad (7)$$

The values of g' and g'' calculated from the curves in Fig. 3 are displayed in Fig. 9 vs. the organoclay content, w .

The Maxwell linear viscoelastic liquid model predicts the values of $g' = 2$ and $g'' = 1$. For lightly crosslinked gels the limiting slopes $g' = g'' = 0$. Thus, the magnitude of these parameters provides an indication about the degree of structure formation, related to clay dispersion.

Fig. 9. The initial slope of the storage and loss moduli increase with frequency, g' and g'' , respectively as functions of the organoclay content, w . The magnitude of experimental error is indicated.

The experimental values of g' and g'' for the matrix polymers are slightly smaller than theoretically predicted. Upon incorporation of clay, they decrease with the solid content. Similar behavior was reported for other PNC. Thus, Lim and Park (24) obtained for the matrix PS: $g' = 1.81$ and $g'' = 0.98$, decreasing upon incorporation of 10 wt% organoclay to $g' = 0.83$ and $g'' = 0.90$. Similarly, Mitchell and Krishnamoorti (22) reported $g' = 1.85$ for PS-PI block copolymer and $g' = 0.6$ for PNC with 5 wt% organoclay. In the latter case, only PS-block was able to intercalate the organoclay, and the immiscibility between the two blocks was mainly responsible for the formation of 3D structure.

The decrease of the initial slope, g' and g'' , is caused by the increase of G' and G'' at the lowest frequencies, which results from the formation of a 3D structure. In PNC, such a structure originates from interaction between the clay platelets within the matrix. When the clay platelets are exfoliated, the effective aspect ratio reaches its maximum and possibility of contact is high, even at the usual low organoclay content of ca. 2 wt%. The interactions are further increased if the platelets are end-tethered with entangling macromolecules. By contrast, when clay platelets are dispersed in the matrix polymer as stacks, the interactions are small and the system behaves like a suspension of solid particles with low $[\eta]$. Therefore, the values of the initial slope may be considered as one of the indicators of the degree of clay dispersion in PNC.

To analyze quantitatively the η' vs. ω dependence, the data were fitted to the Carreau-Yasuda equation (45):

$$\eta' = \eta_0 [1 + (\omega\tau^*)^{m_1}]^{-m_2}; \text{ where: } m_1 m_2 = 1 - n_v \quad (8)$$

In Eq 8, η_0 is the zero shear viscosity, τ^* is the prime relaxation time and m_1 , m_2 are material parameters dependent on polydispersity of molecular weight. In the high deformation rate region, $\omega\tau^* \gg 1$, power-law flow is observed with the power-law index: $n_v = 1 - m_1 m_2$. Similar dependence may also be used to describe the ψ vs. ω dependence with the principal parameters being ψ_0 and the power-law exponent, $n_s = 2 - m_1 m_2$. The computed parameters are listed in Table 4. The square of the correlation coefficient, r^2 , is also given—

it is noteworthy that its values are similar for neat resin and the PNC. In the case of exfoliated or highly intercalated PNC, at low frequencies, the dynamic (28) or complex viscosity (46, 47) increases with decreasing frequency, following different dependence from that given by Eq 8.

The zero-shear viscosity increases with molecular weight of PS. Using the M_w values from Table 1 and η_0 from Table 4, η_0 (kPa·s) = $4.47 \times 10^{-11} M_w^{4.65}$ was found with the correlation coefficient squared, $r^2 = 0.999$. Alternatively, one may compute $\eta_0 = \eta_0(M_w, w)$ using all data from Table 4—in this case the molecular weight exponent is 4.806 ± 0.236 and the frontal factor increases with organoclay content, w . Since the expected value for the exponent is 3.4, the values of M_w in Table 1 may be suspect. From η_0 of Table 4, the values: $[\eta] = 4.8, 4.0$ and 3.3 was calculated from Eq 5 for PS1510, PS1301 and PS1220, respectively, indicating decreasing degree of dispersion with M_w . These values are in qualitative agreement with $[\eta] \leq 4$ calculated from the strain sweep data (see Fig. 8).

The dynamic flow data were also determined for a solution-intercalated sample (PS1301 with 2 wt% C10A). In the absence of degradation, the addition of organoclay enhanced the viscosity by 79% (to be compared with reduction by 40% caused by melt-compounding) indicating that the hydrodynamic volume of the dispersed particle is $[\eta] = 96$. The latter value leads to estimated aspect ratio of the dispersed entities of $p = 269$, quite comparable to $p = 287$ obtained for the well-exfoliated PNC in PA-6 matrix (28), and significantly larger than $p = 16$, calculated for melt-compounded PS-based PNC. The initial slopes for the solution intercalated specimen, $g' = 1.33$ and $g'' = 0.826$ are also significantly smaller than those for melt intercalated ones, viz. 1.80 and 0.98, respectively. Consequently, better dispersion of clay platelets is expected in the solution-intercalated sample than that in the melt-compounded one.

Fourier-Transform Rheology (FTR)

Fourier transform rheology (FTR) was developed by Wilhelm for the analysis of non-linear viscoelastic

Table 4. Parameters for Dynamic Viscosity and the Storage Modulus Coefficient.

Polymer	Organoclay w (wt%)	η_0 (kPa·s)	n_v (—)	ψ_0 (kPa·s ²)	n_s (—)	r^2
PS1510	0.00	4.45	0.138	3.94	0.175	0.99964
	2.10	4.62	0.164	4.62	0.187	0.99990
	6.00	5.07	0.131	4.24	0.217	0.99985
	10.6	5.39	0.136	7.52	0.080	0.99996
PS1301	0.00	8.86	0.110	12.8	0.208	0.99965
	2.80	8.99	0.138	14.1	0.225	0.99993
	5.70	9.18	0.096	11.46	0.194	0.99987
	10.6	10.44	0.110	23.33	0.141	0.99981
PS1220	0.00	17.90	0.104	62.65	0.165	0.99979
	2.50	18.89	0.126	89.45	0.174	0.99990
	5.60	19.47	0.098	87.06	0.157	0.99981
	11.1	20.86	0.084	93.82	0.186	0.99986

Fig. 10. Relative intensity of the third harmonic peak for PS1220 with 10 wt% C10A as a function of frequency and strain at $T = 200^\circ\text{C}$. The input frequency was 6.28 rad/s. Solid points are experimental, the open symbols are calculated from Eq 10.

response in polymeric systems (38). The FTR is capable of measuring the higher harmonics that in the past were qualitatively characterized by, e.g., the Lissajou stress-strain loops. Owing to the complexity of rheological behavior of PNC, FTR was used to describe the nonlinear viscoelastic behavior of PNC based on PA-6 (48).

The FTR analysis shows that the stress is given by a sum of odd harmonics:

$$\sigma \propto A_1 \cos \omega t + A_3 \cos 3\omega t + A_5 \cos 5\omega t + \dots \quad (9)$$

Examples of data observed in the Fourier space are presented in Fig. 5. Under the same temperature and frequency, increasing the strain causes increase of the viscoelastic non-linearity, evidenced by growing magnitude of the higher harmonics, viz. 3rd and 5th. The simplest method of FTR data quantification is to plot the relative magnitude of the odd harmonic peaks divided by the first: $R_n = I(n\omega)/I_1(\omega)$, with $n = 3, 5, 7, \dots$. For linear viscoelastic fluids $R_{n>1} = 0$, whereas for nonlinear materials $R_n = 1/n$, thus the strongest third harmonic, R_3 , contains all information. Figure 10 displays the strain-dependent increases of R_3 for PS1220 and its nanocomposites containing 2.5 and 11.1 wt% of C10A (nominal organoclay loading 2% and 10%).

Wilhelm showed that the strain dependence of $R_3(\omega)$ may be described by one of these two relations:

$$R_3(\omega) = R_{\max} [1 - \exp \{-(\gamma - \gamma_L)/k\}]; \gamma > \gamma_L$$

or

$$R_3(\omega) = a \left[1 - \frac{1}{1 + (b\gamma)^c} \right] \quad (10)$$

where $R_{\max}$ is a measure of the maximum relative intensity, γ is the applied strain, γ_L is the maximum strain for the linear viscoelastic response, while a , b , c , and k are parameters. The first relation was used to determine the limit of the viscoelastic linearity (see Table 5). The second relation provides a better description of the dependence in the whole range of strain. The analysis indicates that the limiting strain for the linear viscoelastic behavior at 6.28 rad/s is common for PS1220 and its PNC containing 2 wt% organoclay. For the PNC sample with 10 wt% organoclay the nonlinearity was observed within the full range of strain—accordingly, $\gamma_L = 0$ was calculated from Eq 10. Furthermore, the expected maximum intensity at high strains is nearly the same for the PS matrix and PNC with 2 wt% organoclay, but incorporation of 10 wt% resulted in high value of $R_{\max}$. Thus, under the test conditions the enhancement of viscoelastic nonlinearity is expected for concentrations exceeding 2 wt% organoclay.

It is noteworthy that at higher strains the curve for 10 wt% sample more or less parallels the dependencies for PS1220 and its PNC with 2 wt% organoclay; thus its viscoelastic nonlinearity may be treated as composed of two parts: the matrix and clay particles dispersed in it. For suspensions of anisometric particles the contribution at low strains and frequency is higher than that at higher frequencies and strains where the aggregates are destroyed and particles are oriented with the stress field. For the well-dispersed, end-tethered clay platelets (e.g., PNC with PA-6 as the matrix) the large aspect ratio of the hairy clay platelets (HCP) induced strong time dependent coupling between the matrix and platelets $R_3(\omega)$ effects (12).

In Fig. 10 the dependence $R_3(\omega)$ vs. γ for the solution-prepared PNC with 2 wt% organoclay is also shown. While for the melt-compounded PNC with 2 wt% organoclay the viscoelastic nonlinearity is the same as that for the matrix polymer, for the solution-prepared specimen the $R_3(\omega)$ values are even higher than those determined for the melt-compounded PNC sample containing 10 wt% organoclay. Furthermore, It has been noted that $R_3(\omega)$ of the solution-prepared PNC continued to increase

Table 5. FTR Parameters for PS1220 and Its Two PNCs.

Parameter	PS1220	PS1220 + 2 wt% C10A	PS1220 + 10 wt% C10A
Standard deviation, σ	0.045	0.046	0.30
Correlation coefficient, r^2	0.9994	0.99999	0.9996
Maximum intensity, $R_{\max}$	79	≈ 90	> 1000
Linear strain limit, γ_L	14.4	14.4	0

with time, indicating a possible progressive exfoliation during the tests.

In summary, FTR provides an easy measure of the viscoelastic nonlinearity, but at low concentration, the degree of dispersion may require time dependence studies at low frequency and high strains (new tooling?). More extensive studies are needed to clarify this point.

Structure-Dependent Strain Hardening, SH

Strain hardening, *SH*, has been observed for long-branch polymers (e.g., LDPE), for highly polydispersed resins (e.g., LLDPE with $M_w/M_n = 10$ to 50) as well as for the new bi-modal metallocene PO. Partial crosslinking as well as dissolution of ultrahigh molecular weight polymer into its standard resin also may induce *SH*.

SH is defined as a logarithmic increment of the stress growth function in elongation over that in linear viscoelastic flow:

$$SH(\varepsilon) \equiv \log(\eta_E^+/\eta_{linear}^+) = \{\log \eta_E^+(\dot{\varepsilon}) - \log [3\eta_S^+(\dot{\varepsilon})]\}_\varepsilon \quad (11)$$

Experimentally, it is customary to substitute: $\log \eta_{linear}^+ = \log [3\eta_S^+(t)]$ at $\dot{\gamma} \leq 0.005 \text{ s}^{-1}$. For single-phase polymers, the plot of *SH* vs. Hencky strain, $\varepsilon = \dot{\varepsilon}t$, does not depend on the strain rate and the value of its slope *SSH*, is a material parameter (49):

$$SSH \equiv \partial SH(\varepsilon)/\partial \varepsilon \quad (12)$$

The value of *SSH* depends on the degree of molecular entanglement—higher entanglement engenders stronger strain hardening. For example, *SSH* for LDPE is about 0.26, thus twice as large as that for PS.

Elongational behavior of multiphase polymeric systems depends very much on the nature of the dispersed phase. For deformable polymer blends, the extensional behavior is non-additive, but the character of flow resembles that of blends components. However, owing to the disturbance of the stress distribution by suspended solid particles, the extensional flow of classical composites shows not *SH*, but its opposite, strain softening (50). For these reasons, the extensional behavior of nanocomposites is of particular interest. Will the clay particles act as solid bodies in the sense of classical composites or will they behave as temporary crosslinks boosting the *SH* behavior of the matrix?

Extensional flows are conceptually the simplest, but they are experimentally the most difficult to perform. They are notoriously time-consuming and prone to numerous errors. Studies of elongational flows of single-phase polymers are rare, and those on PNC are few. Okamoto *et al.* (26) studied the rheology of maleated-PP (PP-MA, 0.2 wt% MAH) and its PNC with 2, 4 and 7.5 wt% of MMT (pre-intercalated with stearyl ammonium ion). The system was only intercalated, with interlayer spacing of organoclay increased from $d_{001} \approx 2.31$ to 3.24, 3.03 and 2.89 nm, respectively. The authors used Meissner-type RME rheometer at $T = 150^\circ\text{C}$ and $\dot{\varepsilon} = 0.001$ to 1.0 s^{-1} . A plot of *SH* vs. ε extracted from published data showed a lack of superposition for different

$\dot{\varepsilon}$, and the slope: *SSH* decreased with increasing strain rate from ca. 5.7 to 0.65, respectively. The lack of superposition originates from a 3D structure, which decreases in its complexity and strength as the deformation rate increase. Considering the exceptionally high *SSH* values, one may speculate that at least some of the structure originates from the PP-MA matrix resin.

Kotsilkova (27) studied flow and birefringence of poly(methyl methacrylate), PMMA, with 10 or 15 wt% of smectite pre-intercalated with methyl di-ethyl propylene glycol ammonium ions. The PNC were reactively prepared. The elongational viscosity and birefringence were measured at 180°C , using a rotating clamp, opto-rheometer designed by Kotaka at $\dot{\varepsilon} = 0.01$ to 1.0 s^{-1} and strains $\varepsilon = 0.8$ to 3. The author noted a correlation between *SH* and birefringence—as the former increased so did the latter. In these systems only a trace of *SH* was observed for PMMA—the effect was quite strong for 10 wt% organoclay, further increasing for 15 wt%. The extracted *SH* vs. ε dependence indicated superposition of data for different strain rates and *SSH* = 0.23 and 0.26 for 10 and 15 wt% organoclay. Thus, these data resembled behavior of entangled single-phase polymers, e.g., that of LDPE.

Turning now to the PS-based PNC studied in this work, the data were collected in RER and in RME. In RER, the linear viscoelastic behavior was observed up to the critical Hencky strain, ε_{cr} , above which an apparent strain softening was observed. Its magnitude was independent of $\dot{\varepsilon}$, slightly increasing with clay content, viz. $\varepsilon_{cr} = 1.84 \pm 0.05$; 1.94 ± 0.02 and 2.02 ± 0.02 , for PS1220 and its PNC containing 2 and 10 wt% organoclay. Owing to specimen sagging in the oil bath, the deformation (especially at higher strains) was nonuniform and the results unreliable.

By contrast with RER results, those from RME indicated *SH* for all specimens, including PS1220 (viz. Figs. 7 and 11). As shown in Table 6, the *SH* started at lower strains than ε_{cr} in RER, thus the two instruments give different results—no *SH* in RER within the strains higher than their onset in RME. Two mechanisms may explain the difference: difference in platelets orientation in the transfer moldings for RER than that in compression molded bars for RME (unlikely), and diffusion of silicone oil into PS matrix (highly probable).

In summary, the extensional flow of PS-based PNC demonstrates that the clay particles have small structure-forming ability—instead of increasing *SSH* (as observed by Kotsilkova (27)) or forming 3D structures that may be progressively destroyed by increasing deformation rate (as reported by Okamoto *et al.* (26)); here, addition of 2 wt% organoclay does not show any effect, while incorporation of 10 wt% reduces *SSH*. Clearly, the PS-based PNC seems to be on the border between the well exfoliated, HCP-type nanocomposites and solid-filled polymer melts with strain softening behavior.

Time-Temperature Superposition (t-T)

For single-component systems, the horizontal, a_T , and vertical, b_T , shift factors are given as (33):

Fig. 11. Strain hardening at $T = 200^\circ\text{C}$ for PS1220 containing 10 wt% organoclay at Hencky strain rate of $\dot{\epsilon} = 0.074$ to 0.899 s^{-1} . The dependence can be approximated by straight line with the slope $\text{SSH} = 0.11 \pm 0.03$.

$$a_T = (\eta_0/\rho T)_T/(\eta_0/\rho T)_{T_{\text{ref}}}; b_T = (\rho T)_{T_{\text{ref}}}/(\rho T)_T \quad (13)$$

$$\therefore a_T = b_T \eta_{0,T}/\eta_{0,T_{\text{ref}}}$$

where, ρ is density, T is temperature and T_{ref} is the reference temperature. The vertical shift factor, b_T , corrects for the volume expansion with temperature, whereas the horizontal shift factor, a_T , for the volume as well as zero shear viscosity. When the t - T superposition is carried out at temperatures below the melting point, e.g., $T_g < T < T_m$, additional vertical shift factor, l_T is usually needed to account for the temperature dependent variation of the crystalline structure and content.

The experimental values of a_T and b_T for the PNC based on the three PS resins are listed in Table 7. The factor a_T decreases with T , but it is almost independent of the PS matrix and organoclay content. The mean value of $a_T = 0.129 \pm 0.007$ and 33.00 ± 3.35 at 240°C and 160°C , respectively. These results are in qualitative agreement with results for PNC based on PP (18) or PS-PI copolymer (21). Values of the vertical shift factor $b_T \approx 1.00 \pm 0.05$, decrease slightly with temperature, viz. $b_T = 0.958 \pm 0.047$ and 1.115 ± 0.058 at 240°C and

Table 6. The Minimum and Maximum Value of Strain Hardening (SH) for PS1220 and Its PNC With Nominal 2 and 10 wt% Organoclay.

System	$\dot{\epsilon}$	$\epsilon_{\min}$	$\epsilon_{\max}$	SSH
PS1220	0.0880	1.58	3.17	0.13 ± 0.03
	0.182	1.64	—	
	0.317	1.53	3.80	
	0.536	1.61	3.75	
PS1220 + 2 wt% C10A	0.0720	1.63	5.47	0.13 ± 0.02
	0.167	2.01	4.01	
	0.430	1.54	6.32	
	0.860	1.85	5.85	
PS1220 + 10 wt% C10A	0.074	1.41	4.55	0.11 ± 0.03
	0.269	1.08	5.38	
	0.453	0.91	5.89	
	0.899	1.08	5.94	

160°C , respectively, and are in good agreement with those computed from the pressure-volume-temperature (PVT) measurements of PS1301: $b_T = 0.945$ and 1.067 , respectively (51).

Near the glass transition temperature, $T_g < T (^\circ\text{C}) < T_g + 100$, the temperature dependence of a_T for polymer melts can be described in terms of the Williams-Landel-Ferry (WLF) equation:

$$\ln a_T = \frac{-c_1(T - T_0)}{c_2 + (T - T_0)} \quad (14)$$

where T_0 is a reference temperature and c_1 and c_2 are the materials constants. When $T_0 = T_s \approx T_g + 50^\circ\text{C}$ the “universal” values of $c_1^s \approx 8.86$ and $c_2^s \approx 101.6$ are observed (33). The data in Table 7 are well approximated by Eq 14 with $c_1 = 3.179$ and $c_2 = 153.43$ for $T_0 = 200^\circ\text{C}$. These values can be converted to the “universal” reference temperature, $T_s = T_g + 50^\circ\text{C}$, giving: $c_1^s = 4.72$ and $c_2^s = 103.4$ (to be compared with $c_1^s = 6.85$ and $c_2^s = 100$ cited by Ferry for PS).

By contrast with polymer blends, in PNC the t - T superposition has been universally observed. As long as the organoclay/matrix system is miscible, and hence reasonably dispersed, the superposition in the molten state is to be expected. A corollary suggests that lack of the t - T superposition should be taken as an indication of phase separation, for example as observed in PO-type PNC, when an inappropriate maleated compatibilizer was used.

Table 7. The Time-Temperature Shift Factors, a_T and b_T at 240°C and 160°C for the PS-Based PNC*.

Polymer	Organoclay w (wt%)	a_T at 240°C	a_T at 160°C	b_T at 240°C	b_T at 160°C
PS1510	0.00	0.131	28.9	0.903	1.086
	10.6	0.136	31.6	1.000	1.030
PS1301	0.00	0.132	34.7	0.926	1.140
	10.6	0.135	32.2	1.000	1.205
PS1220	0.00	0.125	38.7	0.918	1.105
	11.1	0.118	31.9	1.000	1.122

Note: * By definition at $T = 200^\circ\text{C}$ $a_T = b_T = 1.000$.

CONCLUSIONS

The main objective of this study was to examine diverse rheological methods for the characterization of polymeric nanocomposites, PNC. For this purpose a variety of rheological tests were applied, including dynamic and steady state shear flow within the linear and non-linear viscoelastic modes of deformation. Similarly, extensional flow behavior was evaluated in two rheometers to study linear deformability as well as strain hardening.

The object of the study was a series of PNC specimens, prepared by melt compounding in a twin-screw extruder. Three commercial polystyrene resins with different molecular weights were used to prepare PNC with a commercial organoclay. As the results presented in the preceding part indicated, the organoclay as well as the polymeric matrix degraded during the compounding (without N₂ blanket). The clay platelet dispersion in the products was quite heterogeneous, with large aggregates of degraded organoclay, other aggregates with expanded interlayer spacing as well as well-dispersed individual clay platelets. Furthermore, since there is little if any bonding between the PS and the organoclay (MMT intercalated with di-methyl-benzyl hydrogenated tallow ammonium chloride), even with the best dispersion the rheological effects would be significantly smaller than these observed for the end-tethered PNC's.

The results of this study are discussed from the perspective of three topics: detection and characterization of platelet dispersion, characterization of structure existing in the molten PNC, and detection of miscibility of the system

1. Two rheological measures can be used to detect and numerically quantify the degree of dispersion: the first being the intrinsic viscosity, $[\eta]$, and the second is the initial slope of the dynamic shear moduli, g' and g'' . Since $[\eta]$ may be extracted from strain or frequency sweeps and in turn it can be used to calculate the effective aspect ratio of dispersed entities, this measure is favored. The parameters: g' and g'' provide a qualitative measure of 3D structure created by dispersed clay platelets under oscillatory shear flow. In accord with the XRD data, the rheology also shows little difference of the clay dispersion in the three PS grades. However, $[\eta]$ indicates that organoclay dispersion decreases with increase of PS molecular weight.
2. The data from steady state capillary flow experiments superimposed on dynamic viscosity data within the power-law region: $\eta(\dot{\gamma}) \cong \eta'(\omega)$. These tests are useless for characterization of PNC structure.
3. Fourier-transform rheology (FTR) is a powerful tool for studies of the non-linear viscoelastic effects. Since these originate from the presence of 3D structures, FTR can be used to quantify them. However, the danger is that imposition of sufficiently large strain and frequency (to obtain strong harmonic signals) may destroy fragile structures

in some PNC. FTR characterization should be carried out in a range of these variables. In the case of PS-based PNC, the non-linearity of the matrix dominated the behavior with organoclay providing incremental increase at loadings exceeding 2 wt%.

4. The time-temperature (t - T) superposition principle has been shown to be valid for several PNC systems. Good superposition was also obtained for the PS-based PNC. Experimental values of the vertical shift factor agreed numerically with the values computed from the PVT behavior (discussed in the preceding part). The horizontal shift factor was found to follow the WLF dependence, with the values of "universal" c_1^* and c_2^* parameters close to those cited for PS by Ferry. The t - T superposition indicates that within the range of $T = 160^\circ\text{C}$ to 240°C there are no additional temperature-activated processes in the PNC samples—the system behaves as a single-phase polymer melt.
5. Incorporation of up to 10 wt% of organoclay into the three PS resins resulted in a small and similar in magnitude increase of the rheological signal. Detailed analysis of the dynamic flow data indicate that the increase was most pronounced for PNC based on PS1501 with the lowest molecular weight. This may suggest that the intercalation was diffusion controlled, not by mechanical peeling mechanism described for the melt exfoliation in PA-6 matrix (46).
6. The effects of clay addition were observed only at the organoclay loading exceeding 2 wt%. They were the most pronounced at low deformation rates, indicating formation of 3D structures.

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