Viscoelasticity and flow behavior of irradiation grafted nano-inorganic particle filled polypropylene composites in the melt state

To cite this article: V.P. Privalko et al 2002 Sci. Technol. Adv. Mater. 3 111

View the article online for updates and enhancements.

Related content
- The effect of modified juk fibers to crystallinity of polypropylene composite
  I Prabowo, J Nur Pratama and M Chalid

- Environmental Particle Emissions due to Automated Drilling of Polypropylene Composites and Nanocomposites Reinforced with Talc, Montmorillonite and Wollastonite
  K Starost, E Frijns, J V Laer et al.

- Characterization of Polypropylene Composite Reinforced with Wood Flour or Cellulose Fiber
  I Risnasari, E Herawati and E. N Sirait

Recent citations
- Rheological investigation of polyamide 6 TiO2- and BaSO4-nanocomposites
  Irene Hassinger and Thomas Burkhart

- Development of nanocomposite based on hydroxyethylmethacrylate and functionalized fumed silica: mechanical, chemico–physical and biological characterization
  Antonella D’Agostino et al

- Swelling properties and bioactivity of silica gel/pHEMA nanocomposites
  A. Costantini et al
Viscoelasticity and flow behavior of irradiation grafted nano-inorganic particle filled polypropylene composites in the melt state

V.P. Privalko\textsuperscript{a,*}, V.F. Shumsky\textsuperscript{a}, E.G. Privalko\textsuperscript{a}, V.M. Karaman\textsuperscript{a}, R. Walter\textsuperscript{b}, K. Friedrich\textsuperscript{b}, M.Q. Zhang\textsuperscript{c}, M.Z. Rong\textsuperscript{c}

\textsuperscript{a}Institute of Macromolecular Chemistry, National Academy of Sciences of Ukraine, 02160 Kyiv, Ukraine
\textsuperscript{b}Institute for Composite Materials (IVW) Ltd, University of Kaiserslautern, D-67663 Kaiserslautern, Germany
\textsuperscript{c}Key Laboratory for Polymeric Composite and Functional Materials of the Ministry of Education, Zhongshan University, Guangzhou 510275, People’s Republic of China

Received 14 May 2001; revised 14 December 2001; accepted 17 December 2001

Abstract

Nanoparticles (mean size about 7 nm) of the standard pyrogenic Aerosil 1380 (Degussa) pregrafted by $\gamma$-irradiation with styrene were melt-compounded with the general purpose isotactic polypropylene homopolymer to prepare four nanocomposites with filler volume contents up to 4.68%. Storage $G'(\omega)$ and loss $G''(\omega)$ shear moduli in the melt state (measured in the range of linear viscoelasticity at three temperatures in the frequency window spanning about three decades) were treated to derive the relaxation times spectra $\ln(t)$ using the NLREG computer program based on Tikhonov’s method of non-linear regularization.

The experimental data were interpreted in terms of the tentative model highlighting the structural significance of the ratio of mean thickness of polymer interlayer between neighboring filler particles, $(L)$, to the mean radius of gyration of a polymer coil, $(R_g)$. In the range of very low filler loadings characterized by large scaled distances, $(L)/(R_g) \geq 1$, all nanocomposites behaved as Newtonian liquids in which the self-diffusion of macromolecular coils was, however, slowed down. The onset of plastic yield phenomenon for a nanocomposite with the filler volume content as low as 4.68% was regarded as the experimental evidence for the shear-resistant, infinite cluster of filler particles coated with polymer boundary interphase when the scaled distance approached the ‘critical’ value, $(L)/(R_g) \lesssim 1$. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Viscoelasticity; Newtonian liquids; Nanoparticles

1. Introduction

In technological practice, the incorporation of disperse inorganic fillers has long been (and still is) the most straightforward approach to improve the mechanical performance of thermoplastic polymer materials (TPM). This pragmatic idea was theoretically justified by various idealized hydrodynamic models assuming random distribution of isolated, spherical filler particles within a continuous, structureless polymer matrix e.g. Ref. [1]. As predicted by these models, the reduced hydrodynamic properties $P^* = P(\varphi)/P(0)$ (such as the apparent shear viscosity, shear moduli, etc.), in fact, continuously increased with the filler volume fraction $\varphi$; however, a common feature of the relevant data available, e.g. Refs. [2–4], was a considerable ‘overshoot’ of the experimental values of $P^*$ above the theoretical predictions. This effect was tentatively attributed [4,5] to an apparent increase in the volume fraction of the disperse phase due to formation of non-deformable shells (‘boundary interphase’, BI) of a sterically immobilized polymer around the filler particles. Moreover, it was established experimentally [6–8] that all kinetic and thermodynamic properties of the filled TPM exhibited drastic changes at the characteristic filler content $\varphi^*$ at which the effective thickness $(L)$ of the polymer interlayer between neighboring filler particles became comparable with the mean radius of gyration of an unperturbed macromolecular coil $(R_g)$. This result was in a gratifying agreement with theoretical predictions [9]. Thus, the mean size of a polymer coil, $(R_g)$, emerged as a basic structural parameter of filled TPM at the meso- (or nano-) scale.

In this context, the traditional, ‘geometrical’ criterium of a ‘highly loaded’ TPM, $\varphi/\varphi_{\text{max}} \rightarrow 1$, should be complemented by another, ‘structural’ criterium, $(L)/(R_g) \rightarrow 1$...
development of thermoplastic nanocomposites (TPNC) reinforced by relatively small amounts of ultrafine, nanodisperse particles of a few nm in size, which exhibited a dramatic improvement in the stiffness/toughness ratio, gas-barrier properties, flame retardance, etc. [10,11]. In view of these outstanding properties of TPNC, their further development and characterization are considered, on line with other areas of nanotechnology, as one of the major goals of the materials science in the oncoming millenium.

As could be inferred from the previous studies [2–4], the viscoelastic behavior of molten TPC was strongly affected by polymer–filler interactions; however, up till now no quantitative characterization of the relaxation times spectra of TPNC was available. It is, therefore, the purpose of the present paper to report on the viscoelastic properties and relaxation times spectra in the melt state of the TPNC based on polypropylene.

2. Experiment

2.1. Materials

Methods of sample preparation are described in detail elsewhere [12]; therefore, only essentials will be mentioned here. Nanoparticles of the standard pyrogenic Aerosil 1380 (Degussa; mean particle size $d \approx 7$ nm) pregrated by $\gamma$-irradiation with styrene, were melt-compounded at 473 K with the general purpose isotactic polypropylene (PP) homopolymer (grade F 401, melt flow index MFI = 8.5 g/10 min) by a single-screw extruder. In this fashion, TPNC with filler volume contents of 0, 0.39, 0.65, 1.96 and 4.68 (samples PP-0, PP-0.39, etc.) were obtained.

2.2. Method

Storage $G'\!(\omega)$ and loss $G''\!(\omega)$ shear moduli were measured with the PIRSP-03 rheometer [13] in the range of linear viscoelasticity (amplitudes of harmonic vibrations on the order of 1%) at three temperatures (453, 473 and 493 K) in the frequency window spanning about three decades ($\omega = 10^{-2}$–10 rad/s).

3. Results and discussion

As expected, for all studied samples the loss moduli $G''\!(\omega)$ were considerably higher than the storage moduli $G'\!(\omega)$; moreover, both $G'\!(\omega)$ and $G''\!(\omega)$ exhibited a smooth increase with frequency $\omega$ at fixed temperatures (Fig. 1), and a smooth decrease with temperature at fixed frequencies.

The internal self-consistency of the experimental data for PP-0 was proved by construction of master plots (Fig. 2) in which the same values of the shift factor ($a_{\gamma} = 2.0$) were used for both $G'\!(\omega)$ and $G''\!(\omega)$. Another test for self-consistency of the raw data provides the $G'\!(\omega)$ vs. $G''\!(\omega)$ plots.

Fig. 1. Frequency dependencies of the storage (a) and loss (b) shear moduli.

$\langle L \rangle \approx \langle d \rangle (\varphi) / (\varphi)^{1/3} - 1$.

$\langle L \rangle \approx (\varphi) / (\varphi)^{1/3} - 1$, it is clear that the latter condition, $\langle L \rangle / (\varphi)^{1/3} \rightarrow 1$, may be achieved by two alternative approaches. The first (traditional) approach relies on the continuous increase of the filler volume fraction $\varphi$, while the second (so far, largely neglected) one assumes the continuous decrease of the filler particle size $\langle d \rangle$. In so far as $\varphi$ and $\langle d \rangle$ enter Eq. (1) as one-third and first powers, respectively, it becomes obvious that the latter approach to arrive at the structural meso-scale in a TPM should be much more effective. This is essentially the major reason for a significant increase of, say, elasticity moduli and concomitant decrease of thermal expansivities of filled TPM, the smaller the particle size at the same filler loading [5].

Apparently, these and similar observations prompted the
[14]. The excellent linearity of this plot (Fig. 3a) for the neat polymer, PP-0, combined with its reasonably high slope (~0.87), are the typical features for the shear flow of polymer melts far above the glass transition temperature [15].

As could be inferred from the approximate constancy of complex viscosity $|\eta^*| = [(G'/\omega)^2 + (G''/\omega)^2]^{1/2}$ over the fairly broad frequency intervals (Fig. 4), in the range of low frequencies all studied samples (except PP-4.68) behaved as Newtonian liquids. The apparent activation energies for viscous flow estimated from the Arrhenius (ln $\eta^*$ vs. $1/T$) plots, exhibited a slight decrease from $\Delta E/k = 6.6 \times 10^3$ K for PP-0 to $5.1 \times 10^3$ K for PP-0.39, PP-0.65 and PP-1.96. For these samples, the $G'(\omega)$ vs.

$G''(\omega)$ plots also turned out reasonably linear, although the corresponding slopes decreased to about 0.75.

In contrast, one can identify at least two frequency intervals with distinctly different behavior for the nanocomposite with the highest filler content (PP-4.68). In the range of lowest frequencies (i.e. at $\omega < 0.1$ s$^{-1}$), both $G'(\omega)$ and $G''(\omega)$ turned out to have nearly identical magnitudes and to be essentially temperature-invariant and only weakly frequency-dependent (Fig. 1); the experimental data exhibited large deviations from linearity on the $G'(\omega)$ vs. $G''(\omega)$ plot (Fig. 3b); the complex viscosity $\eta^*$ tended to increase, as the frequency lowered (Fig. 4). At higher frequencies, $G'(\omega)$ and $G''(\omega)$ started to diverge and to exhibit
dependencies on both temperature and frequency (Fig. 1), although these dependencies proved much weaker than those for the neat polymer; moreover, no evidence for the Newtonian flow behavior could be detected (Fig. 4).

Thus, the above data may be considered [16] as the empirical evidence for existence of a spatial network (‘infinite cluster’ [5]) of filler particles coated with polymer BI in the low-frequency range, and for its plastic yield at higher frequencies. A similar conclusion can be derived from the analysis of $G'(\varphi)/G'(0)$ vs. $\varphi$ plots (Fig. 5): in fact, the enormous (orders of magnitude) overshoot of the experimental points at low frequency above the predictions of all hydrodynamic theories (a few per cent) is an indirect proof for the existence of very thick BI, while the precipitous drop of the $G'(\varphi)/G'(0)$ ratio for the sample PP-4.68 at higher frequency should be attributed to the plastic yield of the infinite cluster of filler particles coated with polymer BI.

The raw experimental data (Fig. 1) were also treated to derive the relaxation times spectra $h(\tau)$ using the NLEGG computer program based on Tikhonov’s method of non-linear regularization [17,18]. Each of the $h(\tau)$ vs. $\tau$ plots for the neat polymer (PP-0) could be represented by a smooth curve exhibiting a relatively rapid decay which set on at the characteristic relaxation times $\tau_1 = 2.0$ (453 K), 1.3 (473 K) and 0.8 s (493 K), respectively (Fig. 6a). The apparent activation energy $\Delta E_r/k = 5.2 \times 10^3$ K for this ‘fast’ process estimated from the Arrhenius ($\ln \tau_1$ vs. $1/T$) plot, turned out comparable to that for Newtonian melt flow (see earlier).

In terms of the reptation model of polymer flow [19], the rapid decay of $h(\tau)$ may be associated with the disentanglement process (i.e. the complete escape of a polymer chain from the ‘virtual tube’ formed by its neighbors) which is characterized by the relevant maximum relaxation time $\tau_{\text{max}} = (h^2)/D$ (here $(h^2)$ is the mean-square, end-to-end distance for an unperturbed chain in the melt state, and $D$ is the self-diffusion coefficient). Using the tabulated value of $(h^2)/M = 0.66 \times 10^{-20}$ m$^2$ [20] and $D = 5 \times 10^{-11}$ m$^2$/s (estimated from the available data [21] for branched polyethylene) as representative for PP in the melt state at 453 K, one derives $M_1 = 1.5 \times 10^4$ as the most probable molar mass of PP fraction responsible for the ‘fast’ ($\tau_{\text{max},1} = \tau_1 = 2$ s) component of the relaxation times spectrum (Fig. 6a). This rough estimate seems quite reasonable for the PP-0 sample used in our studies with the apparent melt viscosity as low as $\text{MFI} = 8.5$ g/10 min.

A common feature of the relaxation times spectra for nanocomposites with moderate filler loadings (i.e. PP-0.39, PP-0.65 and PP-1.96) is the apparent overlap of the initial ‘fast’ component $\tau_1$ for the neat polymer with the ‘slower’ components decaying at significantly longer (by about an order of magnitude) relaxation times $\tau_2$ (Fig. 6b–d). Formally, this effect may be accounted for by an order-of-magnitude-smaller coefficients of self-diffusion $D$ (say, due to distortions of initial ‘virtual tubes’ in the melt by filler particles coated with polymer BI).

A completely different pattern of the relaxation times spectrum was obtained for the nanocomposite PP-4.68 at 453 K (Fig. 6e): at longer relaxation times the initial decay degenerates into a shallow dip at $\tau_{\text{dip}} \approx 15$ s, after which the spectrum passes through a maximum around the characteristic relaxation time $\tau_3 \approx 100$ s. Moreover, one observes strong shifts of these dips to longer relaxation times, the higher the temperature ($\tau_{\text{dip}} \approx 80$ s and 100 s at 473 and 493 K, respectively), suggesting that the final upswings on the corresponding spectra are the

![Fig. 4. Frequency dependencies of the complex viscosities at 453 K. Symbols as in Fig. 1.](image)

![Fig. 5. Dependencies of the reduced storage shear modulus on filler volume content at 453 K.](image)
Fig. 6. Relaxation times spectra for PP-0 (a), PP-0.39 (b), PP-0.65 (c), PP-1.96 (d) and PP-4.68 (e). Symbols as in Fig. 2.
shorter-time tails of ‘ultraslow’ components with maxima at \( \tau_1 \) (experimentally inaccessible).

The observed drastic changes in the patterns of relaxation times spectra for the PP-4.68 (in particular, the absence of decay at the longest relaxation times), are the clear evidence for a shear-resistant, spatial structure (‘infinite cluster’ [5]) of filler particles coated with BI in the PP melt phase. Using Eq. (1) to estimate the mean gap \( \langle L \rangle \) between surfaces of neighboring filler particles, it can be readily shown that the scaled distance \( \langle L \rangle/\langle R_g \rangle \) remains higher than unity for all studied nanocomposites except PP-4.68 for which \( \langle L \rangle \approx 3.5 \text{ nm} \) turned out comparable to the estimated gyration radius of a macromolecular coil, \( \langle R_g \rangle = \left( \frac{6}{\pi^2} \right)^{1/2} = 4 \text{ nm} \) (in calculations, \( \varphi_{\text{p}} = 15\% \) was assumed as the maximum packing fraction of Aerosil particles [22]). Recalling the anomalous behavior of \( G'(\omega) \) and \( G''(\omega) \) at the lowest frequencies referred to earlier (Fig. 1), it seems reasonable to suggest that the ‘ultraslow’ components of the spectra for PP-4.68 (Fig. 6e) are associated with the onset of plastic yield of an infinite cluster of filler particles coated with BI, preceding the macroscopic melt flow.

4. Conclusions

The characteristic features of the viscoelastic behavior of nanocomposites discussed above are consistent with the following model considerations highlighting the structural significance of the scaled distance between filler particles, \( \langle L \rangle/\langle R_g \rangle \). In the ‘dilute suspension’ regime [23] at low-to-moderate filler loadings characterized by large scaled distances, \( \langle L \rangle/\langle R_g \rangle \gg 1 \), all nanocomposites behave as Newtonian liquids in which the self-diffusion of macromolecular coils is, however, slowed down (presumably, due to distortions of initial ‘virtual tubes’ in the melt by finite clusters of filler particles coated with polymer BI). The onset of plastic yield phenomenon for a nanocomposite with the filler volume content as low as 4.68% is regarded as the experimental evidence for the shear-resistant, infinite cluster of filler particles coated with polymer BI in the ‘semi-dilute suspension’ regime [23] when the scaled distance approached the ‘critical’ value, \( \langle L \rangle/\langle R_g \rangle \approx 1 \). It is believed that this model will prove relevant to the problem of optimization of melt processing regimes, as well as to the understanding of other structure-dependent properties of TPNs.

Acknowledgements

This international cooperation with Ukraine was supported by the International Bureau of the BMBF, Germany, Project UKR-005-99. Further thanks are due to the Deutsche Forschungsgemeinschaft, DFG FR 675/40-1.

References

[1] A.Y. Malkin, Rheology of filled polymers, Adv. Polym. Sci. 96 (1990) 69–97.
[2] G.M. Barteniev, N.V. Zakharenko, On the viscosity and flow mechanism of filled polymers, Koll. Zhurn. 24 (1962) 121–127.
[3] G. Kraus, Interactions of elastomers and reinforcing fillers, Rubber Chem. Technol. 38 (1965) 1070–1114.
[4] Yu.S. Lipatov, V.P. Privalov, V.F. Shumsky, Studies of the melt viscosity of filled oligoesters, Vysokomol. Soed. A 15 (1973) 2106–2109.
[5] V.P. Privalov, V.V. Novikov, The Science of Heterogeneous Polymers, Wiley, Chichester, 1995.
[6] N.L. Rymarenko, Melting and non-isothermal crystallization of highly filled polymers, PhD Thesis, Institute of Macromolecular Chemistry, NAS of Ukraine, 1984.
[7] V.P. Privalov, S.S. Demchenko, G.V. Titov, Calorimetric study of interactions between polystyrene and aerosil, Komposit. Polim. Mater. 27 (1985) 72–75.
[8] G.V. Titov, Energy state of macromolecules in the boundary layers of highly filled polymers, PhD Thesis, Institute of Macromolecular Chemistry, NAS of Ukraine, 1993.
[9] A.M. Skvortsov, A.A. Gorbunov, Conformation of macromolecules in filled polymers, Vysokomol. Soed. A 28 (1986) 1941–1946.
[10] G. Lagaly, Introduction: from clay mineral–polymer interactions to clay mineral–polymer nanocomposites, Appl. Clay Sci. 15 (1999) 1–29.
[11] P.C. LeBaron, Z. Wang, T.J. Pinnavaia, Polymer-layered silicate nanocomposites: an overview, Appl. Clay Sci. 15 (1999) 11–29.
[12] M.Z. Rong, M.Q. Zhang, Y.X. Zheng, H.M. Zeng, R. Walter, K. Friedrich, Structure–property relationships of irradiated grafted nano-inorganic particle filled polypropylene composites, Polymer 42 (2001) 167–175.
[13] G.V. Vinogradov, A.Ya. Malkin, E.P. Plotnikova, A.A. Konstantinov, S.K. Krasheninnikov, A.K. Kalapov, V.M. Bogomolov, A.A. Shakhray, B.A. Rogov, Method for complex characterization of the rheological properties of polymer systems, Vysokomol. Soed. A 20 (1978) 226–230.
[14] H.K. Chuang, C.D. Han, Rheological behavior of polymer blends, J. Appl. Polym. Sci. 29 (1984) 2205–2229.
[15] G.V. Vinogradov, A.Ya. Malkin, Rheology of Polymers, Springer, Heidelberg, 1979.
[16] L. Li, T. Masuda, Effect of dispersion of particles on viscoelasticity of CaCO\(_3\)-filled polypropylene melts, Polym. Engng. Sci. 30 (1990) 841–845.
[17] J. Honekamp, J. Weese, Determination of the relaxation spectrum by a regularization method, Macromolecules 22 (1989) 4372–4377.
[18] J. Honekamp, J. Weese, D. Maier, Program: N(ON) Li(NEAR) REG(ULARIZATION) (METHOD), Copyright: Freiburger Materialforschungszentrum F.M.F., 1998.
[19] P.G. De Gennes, Scaling Concepts in Polymer Physics, Cornell University Press, Ithaca, 1979.
[20] A.E. Nesterov, in: Yu.S. Lipatov (Ed.), Properties of Polymer Solutions and Polymer Blends, Handbook on Physical Chemistry of Polymers, vol. 1, Naukova Dumka, Kyiv, 1984 (in Russian).
[21] M. Tirrell, Polymer self-diffusion in entangled systems, Rubber Chem. Technol. 57 (1984) 523–556.
[22] L.B. Kandrygin, V.N. Kuleznev, E.L. Chernin, A.S. Freidin, S.M. Grinberg, On the calculation of elastic moduli of filled polymers at high filler loadings, Koll. Zhurn. 39 (1977) 966–968.
[23] Ye.P. Mamunya, E.G. Privalko, E.V. Lebedev, V.P. Privalko, F.J. Balta Calleja, P. Pissis, Structure-dependent conductivity and micro-hardness of metal-filled PVC composites, Macromol. Symp. 169 (2001) 297–306.