Dynamic Mechanical Properties of Agricultural Residues-Filled Polystyrene

Mahmoud A.-Halim Abdel-Goad

Chemical Engineering Department, Faculty of Engineering, El-Minia University, Egypt

Received 30 September 2003; accepted 3 February 2004
DOI 10.1002/app.20371
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Agricultural residues (cotton straw) were added as very small particles to polystyrene (PS) at different weight ratios by using a melt-mixing technique. The dynamic mechanical tests were performed over a wide range of temperatures and frequencies by using an ARES rheometer (Rheometrics Scientific) operated in the dynamic mode. The dynamic mechanical properties in terms of the storage modulus (G'), loss modulus (G''), compliance moduli, loss tangent, and dynamic viscosity were studied and compared for PS and PS composite. The results showed that the dynamic mechanical moduli and viscosity were found to increase with the addition of cotton straw and rise further with its loading increasing.© 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 37–40, 2004

Key words: agricultural residues; PS composite; melt viscosity

INTRODUCTION

Polymer composites reinforced with short fibers are used increasingly in a variety of industrial applications owing to their high stiffness, high strength-to-weight ratios, and ease of processing. Their properties can be tailored according to the types of reinforced fibers and matrix materials used. The use of natural fibers such as wood, jute, pineapple, sisal, and cotton in polymeric composites have received considerable attention recently. This because wood and cellulosic fiber exhibit several attractive mechanical properties for use as reinforcements in thermoplastics. In addition, they are inexpensive, renewable, degradable, and environmentally friendly.[1–8] Environmental concerns generated by plastic materials are generating increasing interest toward the development of ecological products. The use of disposable plastic materials increases the undegradable portion of waste; for this reason, it is necessary to develop more recyclable and/or biodegradable plastics to reduce the amount of plastic in landfill. Therefore, much R&D work was carried out on biofiber-reinforced synthetic polymers, and the study of polymer composites that contain cellulosic materials was recognized as an important area of research for over the last decade.[9–15]

Dynamic mechanical tests, in general, give more information about a composite material than other tests. Dynamic tests, over a wide range of temperatures and frequencies, are especially sensitive to all kinds of transitions and relaxation processes of matrix resin and also to the morphology of the composites. Dynamic mechanical analysis is a sensitive and versatile thermal analysis technique, which measures the modulus (stiffness) and damping properties (energy dissipation) of materials as the materials are deformed under periodic stress.[16]

The aim of the present study was to contribute to the reduction of pollution by using waste agricultural residues in producing semi-biodegradable composites and analysis of its this composite dynamic mechanically compared to the same material using unfilled polystyrene (PS).

EXPERIMENTAL

Materials

In this study, commercial PS from Aldrich (lot no. CQ09610KN) was used as the matrix. The molecular weight and molecular weight distribution of PS were determined to be ($M_w = 2.83 \times 10^5$ g/mol and $M_w/M_n = 2.03$) by size exclusion chromatography (SEC) analysis (Waters 150C, Millipore, equipped with a differential refractometer detector operated at 25°C with tetrahydrofuran as the mobile phase and PS standard for calibration). The columns were selective for molecular weights between 1000 and 10^7 g/mol. The fiber utilized in this work was cotton straw. The cotton straw was dried and shredded into very small particles: the particle sizes of the straw were in the range of 0.2–0.5 mm as determined by light microscopy in the transmitting mode. The straw was added to the PS in

Present address: Forschungszentrum Juelich-IFF-52428, Juelich-Germany (m.goad@fz-juelich.de).

Contract grant sponsor: International Bureau in Germany.

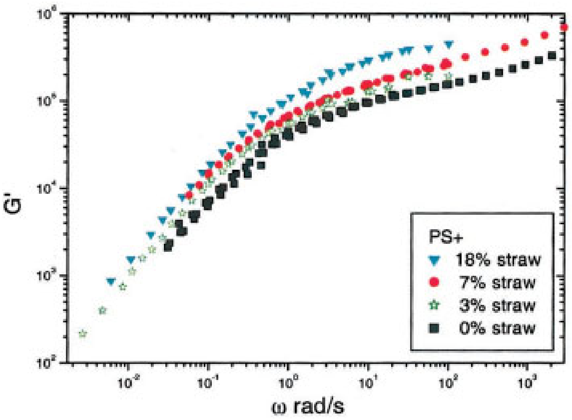

Figure 1 Master curve of G' as a function of ω for filled and unfilled PS at $T_0 = 160°C$.

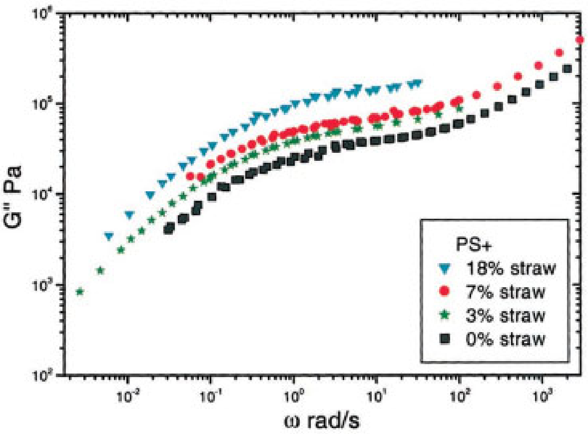

Figure 2 Master curve of G'' as a function of ω for filled and unfilled PS at $T_0 = 160°C$.

different weight fractions (3, 7, and 18%). The mixture was dry mixed homogeneously followed by melt-mixing. Then, samples from filled and unfilled (original material) PS were compression-molded in disc form with a diameter of around 25 mm and a thickness of about 2 mm for the rheology tests.

Measurements

The melt rheological properties of the material were determined by using an ARES rheometer (Rheometric Scientific, USA). In this work, the measurements were performed in the dynamic mode and 25 mm parallel plates geometry with gap settings of about 2 mm. The strain amplitude was kept at 2% over the whole frequency range to ensure linearity. The samples were measured over a wide range of temperatures as a function of frequency. The temperature ranged from 130 to 220°C and the frequency, ω, varied between 10^{-1} and 10^2 radian/s.

RESULTS AND DISCUSSION

The log–log curves of the data measured at different temperatures were superposed into a master curve at a reference temperature T_0, by use of the time–temperature superposition principle. By using the relationship described by Williams–Landel–Ferry (WLF),[17] we introduced a shift factor a_T that permitted data, obtained at some temperature T, to be shifted and reduced to a reference temperature T_0, as $\log a_T = -C_1(T - T_0)/[C_2 + (T - T_0)]$. The constants C_1 and C_2 are material specific. T_0 is chosen in this study to be 160°C. a_T shifts the data obtained at different temperatures along the log frequency, ω-axis, and in the vertical direction, the shifting is given by the ratio of $(\rho T/\rho_0 T_0)$,[18] where ρ is the material density. The vertical shift factors were small and expected.

The master curves of the dynamic moduli for filled and unfilled PS samples at various temperatures are logarithmically plotted against the frequency (angular). The dynamic spectrum of shear storage modulus G' (Fig. 1) and shear loss modulus G'' (Fig. 2) with respect to frequency contain information regarding the manner in which a sample responds to small-magnitude deformation applied over varying temperatures and time scales. It is clear from Figures 1 and 2 that G' and G'' moduli for filled PS are higher than those of unfilled PS and the moduli increase with the filler loading. This may be due to the formation of the polymer–fiber network. The ratio of G''/G' is tan δ and it measures the imperfection in the elasticity. tan δ indicates the relative degree of viscous-to-elastic dissipation of the material. Therefore, tan δ is called the loss factor. tan δ is plotted as a function of frequency for filled and unfilled PS in Figure 3. tan δ is shown to increase with the increase in the filler content as seen in Figure 3.

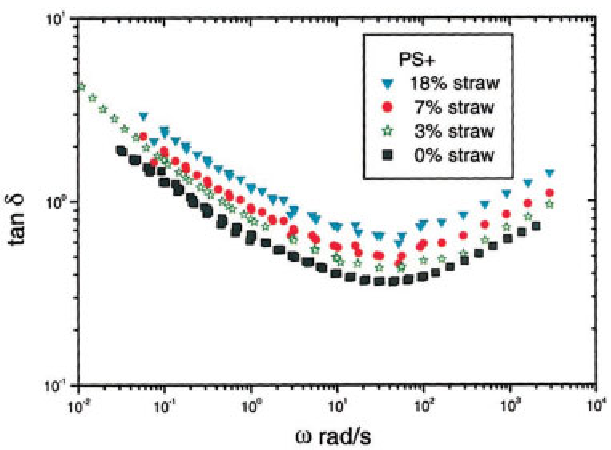

Figure 3 Master curve of tan δ as a function of ω for filled and unfilled PS at $T_0 = 160°C$.

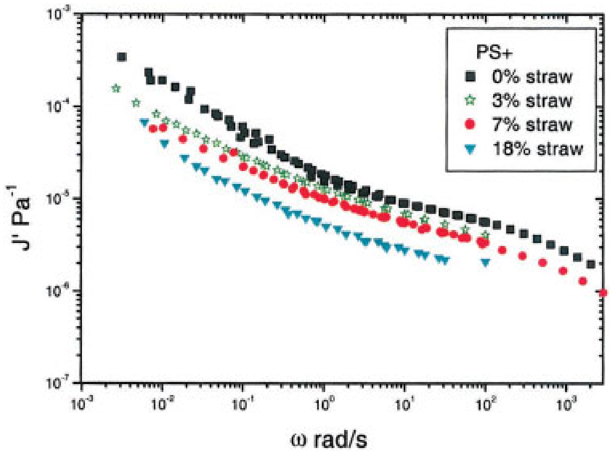

Figure 4 Master curve of J' as a function of ω for filled and unfilled PS at T_0 = 160°C.

The storage, $J'(\omega)$, and loss, $J''(\omega)$, compliance are plotted with logarithmic scale in Figures 4 and 5, respectively. $J'(\omega)$ is a measure of the energy stored and recovered per deformation cycle; therefore, it is called the storage compliance. $J''(\omega)$ is a measure of the energy dissipated as heat per cycle of the sinusoidal deformation and is called the loss compliance. $J''(\omega)$ and $J'(\omega)$ resemble $G'(\omega)$ and $G''(\omega)$, respectively: they have roughly the appearance of a mirror image of $G'(\omega)$ and $G''(\omega)$ reflected in the frequency axis. Again the incorporation of the cotton straw enhances the $J'(\omega)$ and $J''(\omega)$ moduli.

The dynamic viscosity $\dot{\eta}$ is plotted versus ω in Figure 6 and is related to the loss modulus, G'', as $\dot{\eta} = G''/\omega$. $\dot{\eta}$ decreases monotonically with increasing ω and falls by many orders of magnitude as shown in Figure 6. At very low frequencies, $\dot{\eta}$ approaches the zero-shear viscosity, η_0, at which the viscosity is independent of the frequency and η_0 can be obtained from G'' and ω as $\eta_0 = \lim_{\omega\to 0} [G''(\omega)/\omega]$.[19] Figure 6 shows

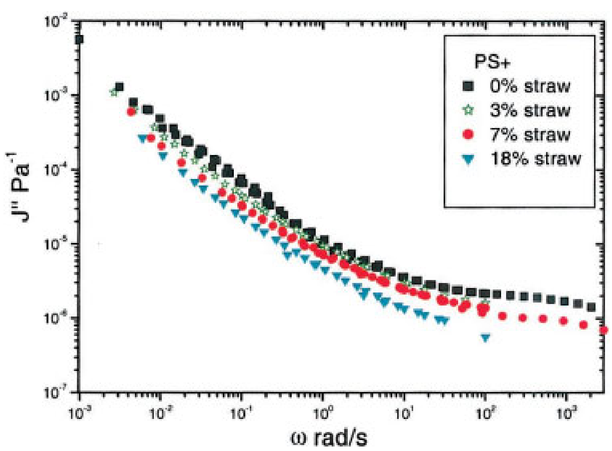

Figure 5 Master curve of J'' as a function of ω for filled and unfilled PS at T_0 = 160°C.

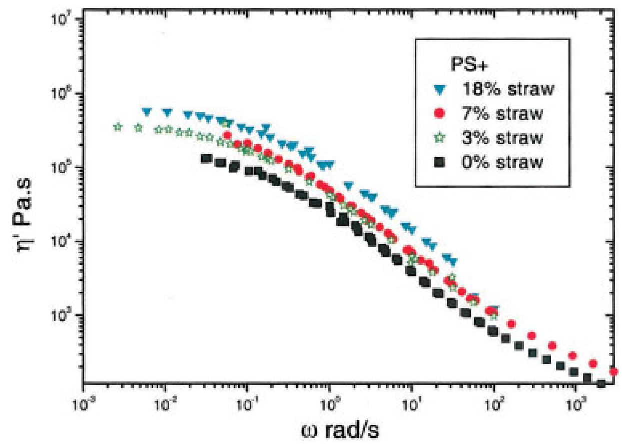

Figure 6 Master curve of $\dot{\eta}$ as a function of ω for filled and unfilled PS at T_0 = 160°C.

an increase in the viscosity for fiber-filled composites and is shown to increase markedly with fiber content, particularly at very low frequencies. The η_0 values for pure PS and PS composites may be compared in Figure 6. We can see, for example, the incorporation of 3 wt % straw into PS results in a significant increase in η_0 at 160°C from about 1×10^5 to 4×10^5 Pa s.

As shown in the Results of this study, the addition of the cotton straw increases the dynamic mechanical moduli and their values tend to increase as the filler loading increases. This is because of the effect of incorporation of a high modulus material fiber into a low modulus amorphous one. Moreover, this is thought to be due to the formation of an immobilized polymer shell around the filler, which is contributing to the overall stiffness and the amount of which becomes significant as the amount of the filler increases.[20] As a result, fiber-filled composites possess unusually high strength and stiffness for a given weight of material and these properties are altered by altering the composition of the fiber–polymer combination. Therefore, the dynamic mechanical moduli and the viscosity increase with increasing fiber content.

CONCLUSION

Polystyrene composites were prepared in this study by a melt-mixing process for commercial PS with cotton straw. The dynamic mechanical measurements for filled and unfilled PS were performed in the dynamic mode and in the parallel plate geometry with 25 mm diameter, over a wide range of temperatures and frequencies by using an ARES rheometer.

The results showed that the dynamic mechanical moduli and viscosity are found to be enhanced with the incorporation of the cotton straw and their values tend to increase as the fiber loading increased. Therefore, fiber-filled composites have much potential for applications of environmentally degradable plastics, owing to their strength and stiffness.

The financial support by the International Bureau in Germany, SEC measurement by Marlies Hintzen, and the helpful discussions of Dr. W. Pyckhout-Hintzen (FZJ, Jülich, Germany) and Dr. Petra Poetschke (IPF, Dresden, Germany) are acknowledged.

References

1. Tjong, S. C.; Xu, Y.; Meng, Y. Z. J Appl Polym Sci, 1999, 72, 1647–1653.
2. Saheb, D. N.; Jog, J. P. Adv Polym Technol 1999, 18, 351–363.
3. Angles, M. N.; Salvado, J.; Dufresne, A. J Appl Polym Sci 1999, 74, 1962–1977.
4. Takase, S.; Shiraishi, N. J Appl Polym Sci 1989, 37, 645–659.
5. Dintcheva, N. T.; La Mantia, F. P. Polym Adv Technol 1999, 10, 607–614.
6. Basu, D.; Banerjee, A. N.; Misra, A. J Appl Polym Sci, 1992, 46, 1999–2009.
7. Maldas, D.; Kokta, B. V.; Daneault, C. J Appl Polym Sci, 1989, 38, 413–439.
8. Kalaprasad, G.; Mathew, G.; Pavithran, C.; Thomas, S. J Appl Polym Sci 2003, 89, 432–442.
9. Mohanty, A. K.; Misra, M.; Hinrichsen, G. Macromol Mater Eng 2000, 276/277, 1–24.
10. Bledzki, A. K.; Reihmane, S.; Gassan, J. J Appl Polym Sci, 1996, 59, 1329–1336.
11. Lowys, M.-P.; Desbrieres, J.; Rinaudo, M. Food Hydrocolloids 2001, 15, 25–32.
12. Felix, J. M.; Gatenholm, P. J Appl Polym Sci 1991, 42, 609–620.
13. Swerin, A. Colloids Surf A 1998, 133, 279–294.
14. Gatenholm, P.; Bertilsson, H.; Mathiasson, A. J Appl Polym Sci 1993, 49, 197–208.
15. Iannace, S.; Nocilla, G.; Nicolais, L. J Appl Polym Sci 1999, 73, 583–592.
16. Saha, A. K.; Das, S.; Bhatta, D.; Mitra, B. C. J Appl Polym Sci 1999, 71, 1505–1513.
17. Ferry, J. D. Viscoelastic Properties of Polymers, 3rd ed.; Wiley: New York, 1980.
18. Pearson, D.; Fetters, L.; Grassley, W. Macromolecules 1994, 27, 711–719.
19. A.-Halim Abdel-Goad, M. Ph.D. thesis, Muenster University, Germany, 2000.
20. Rothon, R. N. Adv Polym Sci 1999, 139, 69–105.