Softwood/Polystyrene Composites Part I: Preparation and Melt Rheology Characterization

Mahmoud Abdel-Halim Abdel-Goad

Chemical Engineering Dept., Faculty of Eng., Minia Uni., Egypt E-mail: m.abdelhalim@mu.edu.eg

Abstract: In this study polystyrene (PS) composites with various compositions were prepared from softwood wastes by melt mixing technique. PS has sufficient high molecular weight (280000 g/mol) was mixed in the molten state with very small particles of softwood. PS composites and PS base were rheologically characterized. The rheological measurements were performed using ARES-rheometer (Rheometric Scientific, USA) in the dynamic mode and parallel plate geometry with diameter 25 mm. The measurements were carried out at temperatures ranged from 140 to 240°C over a wide range of frequencies in the linear viscoelastic regime (strain 1%) and gap setting around 1 mm. The rheological properties such as shear complex modulus, G*, shear storage compliance modulus, shear loss compliance modulus, loss tangent and complex viscosity of PS composites and the original material of PS have been studied and compared. The results showed that the viscoelastic properties are found to be improved by the addition of softwood wastes and their values increase with increasing filler loadings.

Keywords: Polystyrene, softwood wastes, composite, rheology, dynamic mechanical moduli, complex viscosity

1. INTRODUCTION

Fiber-reinforced plastic composites began with cellulose fiber in phenolics in 1908, later extending to urea and melamine, and reaching commodity status in the 1940s with glass fiber in unsaturated polyesters [1].

Fiber-reinforced composites have two things going for them. They are strong and light. They are often stronger than steel, but weight much less. This means that composites can be used to make automobiles lighter, and thus much more fuel efficient. Most of the interest is in aerospace. There is a lot of interest right now in making a spaceplane which can fly from Tokyo to Los Angeles in three hours. This plane would enter a low earth orbit during its flight. That means it would have to re-enter the atmosphere, and re-entry will generate a lot of heat on the surface of airplane. Composites are needed which can stand up to the torture. Filled polymer composites are attracting ever growing interest. Therefore, nowadays the reinforced polymers composites has been recognized as an important area of research [2-15]. Currently considerable interest is focused on PS composites prepared by incorporation of various fillers in PS as reported in the literature by different authors [16-20].

The growth rate of the use of particulate filled polymers is very fast in all fields of application. Household articles and automotive parts are equally prepared from them. In the early stages, the sole reason for the introduction of fillers was to decrease the price of the polymer. However, as a result of filling all properties of the polymer change, a new polymer is in fact created. Some characteristics improve, while others deteriorate, and properties must be optimized to utilize all potentials of particulate filling. Optimization must include all aspects of the composites from component properties, through structure and especially interactions.

Nowadays Mineral fillers and fibers are extensively used in the plastics industry to achieve desired properties or to reduce the price of the finished article [21]. Carbon fiber reinforced composites are very strong for their weight. They are often stronger than steel, but a whole lot lighter. Because of this, they can be used to replace metals in many uses, from parts for airplanes and the space shuttle to tennis rackets and golf clubs. The importance of fiber-filled composites arises largely from the fact that such materials can have unusually high strength and stiffness for a given weight of material. In addition, there is an increasing interest in environmental concerns[21].

The composites of natural fibers and non-biodegradable synthetic polymers may offer a new class of materials but are not completely biodegradable. The designing materials compatible with the environment becomes the target from the government regulations and growing environmental awareness throughout the world.

Since polymer melt flow behaviour is strongly affected by the nature of the filler type, including its morphology, surface chemistry and concentration, rheological studies can also assist in the development of formulations designed to facilitate industrial processability.

Current study will be focused in the preparation of PS composites from high molecular weight PS and softwood wastes with different weight ratios by melt mixing technique and characterize these materials rheologically at a wide range of temperatures above the glass transition temperature of the materials and large frequencies variation.

The adding of softwood residual as filler in preparing PS composites is potenciated to maximize the use of renewable resources and also to minimize the wastes. In addition to, its use as a lightweight and economical source of reinforcement in thermoplastic composites. Therefore it was the motivation of this work is to contribute in the environmental problems by minimizing the wastes and producing recyclable/semi-biodegradable plastic composites by incorporation softwood wastes into polystyrene with high molecular weight. Because the recycling by different methods such as combustion of wood-filled composites "as an example" is easier as compared to plastics alone or with inorganic fillers. Moreover, the aim of this study is to enhance the viscoelastic properties of the polystyrene by adding high specific strength fillers and characterize these properties rheologically.

2. EXPERIMENTAL PART

Materials and Preparation

In this study PS composites were produced by adding softwood wastes to polystyrene with sufficiently high molecular weight of 280000 g/mol (280K). The softwood wastes were dried, shredded and grinded in very small particle sizes of Microns. The fillers were added to PS in different weight ratios (1, 3, 5 and 7 wt%). Composites were prepared by mixing homogenously PS in the molten state with wood wastes followed by casting the samples for rheology tests under press-mould at 300°C and 5 bars for 30 minutes. The samples were shaped in the disc form with diameter around 25 mm and thickness about 1 mm. The samples of the original material of PS base were press-molded also for rheology tests with the same dimensions and press-mould conditions of the composites.

Instrument and Measurements

The rheological behavior was studied using dynamic oscillatory tests. In this test, when a sinusoidal strain is imposed on a linear viscoelastic material, a sinusoidal stress response will result and the dynamic mechanical properties depend upon temperature and frequency.

In this study the measurements were performed by using ARES-Rheometer (Rheometric scientific, USA) over a wide range of temperatures and frequencies, under nitrogen atmosphere, in the dynamic mode and on the parallel plate geometry of 25 mm diameter. The angular frequency ($^{(0)}$) varied from 102 to10-1 radian/s and the temperature ranged from 140 to 240°C. The gap setting was about 1mm and the actual gap size is read electronically and allows absolute moduli to be determined. The strain amplitude was kept in the range 1-2% to ensure linearity. 8 points per decade in frequency were obtained. Horizontal and vertical shift factors were obtained from a two dimensional shifting at chosen reference temperatures.

3. RESULTS AND DISCUSSION

The log -log curves of the data measured at different temperatures were superposed into master curve at a reference temperature, T0, by shifting the experiments data in the horizontal and vertical directions as shown in Figure 1. In this Figure the shear complex modulus (G^*) is plotted for non-shifted and shifted data as a function of frequency. As shown in Figure 1, G^* decreases with increasing the temperature as seen in the case of non-shifted data. The experiments data were shifted into a single curve (master curve) by using of the time-temperature superposition

principle which described by Williams-Landel-Ferry (WLF) [22] as, log $a_T = \frac{-c_1(T - T_0)}{c_2 + (T - T_0)}$. Where a_T is the

empirically derived shift factor and constants C_1 and C_2 are material specific and their values are listed in Table 1. 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 (horizontally) as shown in Fig.1. Since the dynamic mechanical moduli depend on the temperature, therefore the experiments data are shifted also in the vertical direction. The shifting in the vertical direction is given by b_T as, $b_T = \rho T / \rho_0 T_0$ [23]. Where ρ is the material density and the shift factors for these samples, as an example, are plotted with respect to temperature in Figure 2. a_T (Fig2a) decreases by increasing the temperatures up to a certain limit (about 200°C) then becomes somewhat constant independent on the temperature. Unlike b_T is nearly constant up to about 200°C and starts to decreases dramatically after 200°C as shown in Figure 2b. Accordingly, the values of dynamic mechanical moduli decreases at high temperatures.

Polymer	C ₁	C ₂	r ²
PS280K	6.16	94.92	0.98
PS280K+1%RSS	6.19	100	0.95
PS280K+3%RSS	6.41	121	0.91
PS280K+5%RSS	6.63	156	0.88
PS280K+7%RSS	6.85	172.15	0.88

Table 1: WLF constants of PS and PS composites at $T_0 = 160^{\circ}C$

The master curves of the shear complex modulus, G* of PS and PS composites at 160°C are logarithmically plotted against the frequency (angular) in Figure 3. This quantity of G* can be resolved into two components as $G^* = G' + i$ G'' [24]. Where G' is the ability of the material to store energy in the cycle of the deformation and G'' is defined as the ability of the material to dissipate the energy per cycle of the deformation. The dynamic spectrum of shear storage modulus (G') and shear loss modulus (G'') with respect to frequency contains information regarding the manner in which a sample responds to small magnitude deformation applied over varying temperatures and time scale. The stress: strain ratio at any instant in time defines the complex shear modulus as, $G^* = \sigma(t) / \gamma(t) = \sigma e^{i\delta} / \sigma$ γo [24] where γ is the strain, σ is the stress and stress σ , t is time and δ is the phase angle between stress and strain. The master curve of G^* shows three distinct regions of behavior and that is typically for flexible-chain monodisperse homopolymer as, the glass transition, rubbery plateau, and terminal zones when going from high frequency to low frequency. The glass transition zone is the regime in between the glass and rubber-like zones at which the deformation frequency is high as compared to the average relaxation time of the polymer chain. Since some molecular chain segments can not move while some are free to move. If the stress is initially applied, the segment will move in such a manner as to reduce the stress on it. After moving, the segment has less stored energy because of the reduction in stress, so the excess energy was dissipated as heat and the observed modulus is high at high frequencies as shown in Figure 3. As the frequency of deformation decreases, G^* decreases until the intermediate ($\omega \sim 100-1 \text{ rad/s}$) at which the rubber-like regime is found. It reflects the rubber-like properties of the polymer, and indicating that polymer chains have sufficiently time to relax locally but at adequately high molecular weights are entangled and exhibit behavior consistent with a rubbery network. The melt regime is located at very low frequencies ($\omega \le 1$ rad/s) at which G* drops by many order with decreasing the frequencies. Figure 3 shows that G* of the PS composites is higher than this of pure PS and the values of G* are found to rise with increasing RSS content within the experimental range. That is good for materials in a lot of applications to have high moduli and resist deformation. The increase in the moduli by adding the softwood wastes is owing to the formation of the polymer-fiber- network which leads to increase the strength of the PS composite. Numerically at around 50 radians/s the value of G* increased from about 0.14 to 0.18, 0.2, 0.23 and 0.25 MPa by the incorporation of 1, 3, 5 and 7% wt% RSS into PS, respectively. At low frequencies the enhancement in the dynamic mechanical moduli of the shear complex modulus becomes more significant as shown clearly in Figure 4, where at about 10^{-3} rad/s (Fig.4c) the G* of PS+7wt% RSS is about two times more than this of neat PS. The dependency of G* on the filler content is more greater at low frequency than high frequency, since the power law "n" ($G^* \sim \phi^n$, ϕ is the wt% of RSS) increases from about 2 at $\omega = 10^3$ rad/s to 2.3 and 3 at $\omega = 0.5 \times 10^2$ and $\omega = 10^{-3}$ rad/s, respectively. That is related to the disentangled of the PS chains in this regime but the addition of RSS interacts "physically" with the polymer chains resulting in network-like structure which hinders the completely disentanglement of the polymer chains, therefore the stiffness increases. The effect of the RSS on the disentangled chains can be clearly seen and confirmed by replotting G* versus time in Figure 5. This Figure evidences that the relaxation time is enlarged by incorporation of the RSS into PS, since the modulus of the PS composites at long times is kept higher than this of PS base as shown in Figure 5. That reflects the high stability of the composites at long time of deformations.

Similar results reflect the influence of the softwood addition are shown in Figs 6 and 7 for the shear compliance. The storage, $J'(\omega)$ and loss, $J''(\omega)$ compliance are plotted with logarithmic scale in Figures 6 and 7, respectively. $J'(\omega)$ is a measure of the energy stored and recovered in deformation cycle, therefore it is called the storage compliance . $J''(\omega)$ is a measure of the energy dissipated as heat in cycle of the sinusoidal deformation, for that is called the loss compliance and it relates to the energy loss density during one cycle of strain, $\Delta E = \pi \times \sigma_0^2 \times J''$.

The plot of $J'(\omega)$ has roughly the appearance of mirror image of G* plot reflected in the frequency axis. Figures 6 and 7 represent three distinct regions of behavior as explained above for G* modulus. A sign of enhancement is found also by addition of RSS to PS. As an example in Figure 6 at ω equals to100 radian/s the value of J' changed from 8.7×10^{-6} to 4×10^{-6} Pa⁻¹ by the addition of 7% RSS. This is because of the formation of the crosslinked-like, hence the increase in the strength of the PS/RSS composites. In addition to, the incorporation of high specific strength and modulus materials of solid filler leads to increase the stiffness of the composites.

Tan δ of filled and unfilled PS is plotted in Figure 8 as a function of frequency. Tan δ measures the imperfection in the elasticity and it indicates the relative degree of viscous to elastic dissipation of the material. The introducing of the filler into PS increases tan δ and the values of tan δ increases "slightly" by increasing the filler content within the experiments range as shown in Figure 8. This Figure shows also a decrease in tan δ with increasing the frequency followed by increasing again and the minimum of tan δ is in the range of about 25 to 80 radian/s for both of filled and unfilled PS. The minimum in tan δ corresponds to the minimum in loss energy per cycle of the sinusoidal deformation which is related to the rubbery regime where the perfection of the elasticity due to the entanglements of the polymer chains. Tan δ increases by the addition of the fillers as seen in Figure 8.

The complex viscosity η^* is plotted versus ω in Figure 9 and it is related to the dynamic viscosity, η' as, $\eta^* = \eta' - i \eta''$. η^* decreases monotonically with increasing ω and falls by many orders of magnitude as shown in Figure 9. At very low frequencies, particularly in the case of unfilled PS, η^* approaches the zero-shear viscosity , η_0 (Newtonian viscosity branch). Figure 9 shows an increase in the viscosity of PS composites as compared to unfilled PS, particularly is significant in the Newtonian viscosity branch. At about 0.003 rad/s the viscosity of PS rises from about 2.2 ×10⁵ to 2.6 ×10⁵, 3.5 ×10⁵, 3.9 ×10⁵ and 4.7 ×10⁵ Pa.s by the incorporation of 1, 3, 5 and 7 wt% RSS into pure PS, respectively. As shown in Figure 9 the presence of fibers in viscous PS melt not only increases its viscosity but also influences its frequency dependency which alters the beginning of frequencies-independent. As an example, the beginning of frequencies- independent is shifted by the incorporation of 7wt% RSS filler from around 0.05 (in the case of pure PS) to 0.03 radian/s.

The increase in η^* by the addition of RSS gives again evident for the improvement. This increase in the viscosity may be because the decrease in the degree of freedom of polymer chains due to formation of an immobilized polymer chains around the fiber. In addition, the incorporation of the softwood into plastics gives high filling "compactness" resulting in high viscosity. Here, this increase in the viscosity is generally as described by Einstein equation, which predicts the viscosity of a Newtonian fluid containing a very dilute suspension of rigid spheres as, $\eta=\eta_1$ (1+ K_E × ϕ) where η is the viscosity of the mixture, η_1 is the viscosity of the suspending liquid and ϕ is the volume fraction of fillers and K_E is the Einstein coefficient which for spherical particles is 2.5 and vary according to the particle shape and orientation [25].

4. CONCLUSION

In this study PS/softwood composites were prepared by melt-mixing technique. The rheological measurements were performed using ARES-rheometer (Rheometric Scientifics, USA) in the dynamic mode and parallel plate geometry with 25 mm diameter. The measurements were carried out at temperatures ranged from 140 to 240°C and frequencies varied from 0.1 to 100 rad/s at strain 1 % and gap setting 1 mm. The viscoelastic properties in terms of complex modulus, compliance moduli, loss tangent and complex viscosity have been studied and compared for PS composite and the original material of pure PS. The experiments data at different temperatures could be shifted by using WLF principle "sufficient" accurately into a master curve at a reference temperature. In few words, the results showed that the viscoelastic properties are found to be improved by the addition of softwood and their values rise with filler loadings. Therefore, Fiber-filled composites have much potential in a wide range of applications.

5. ACKNOWLEDGMENTS

Helpful discussions of Dr. W.Pyckhout-Hintzen at Research center Juelich, Germany are greatly acknowledged.

REFERENCES

[1] A.K.Mohanty, M.Misra and G.Hinrichsen, Macromol.Mater.Eng, 276/277, P.1-24, 2000.

- [2] Z.Fang and Q.Hu, Die Angewandte Makromolekulare Chemie, V 265, Nr.4474, P. 1-4, 1999.
- [3] K.Mitsuishi, Die Angewandte Makromolekulare Chemie, V 248, P. 73-83, 1997.
- [4] K.M.Lee and C.D.Han, Polymer, V44, P.4573-4588, 2003.

[5] X.Hu et al., Macromolecules, V36, P.823-829, 2003.

Vol. 2 Issue 1, January – 2018, Pages: 65-73

- [6] G.B.Mcginness and C.M.O.Bradaigh, J.Non-Newtonian Fluid Mech., V73, P.1-28, 1997.
- [7] J.I.Kim, S.H.Ryu and Y.W.Chang, J.of Applied Polymer Science, V77, P.2595-2602, 2000.
- [8] J.H.Tavman, J.of Applied Polymer Science, V62, P.2161-2167, 1996.
- [9] M.J.Solomon et al., Maromolecules, V34, P.1864-1872, 2001.
- [10] D.Marchant and K.Jayaraman, Ind.Eng.Chem.Res., V41, P.6402-6408, 2002.
- [11] S.S.Ray, P.Maiti, M.Okamoto, K.Yamada and K.Ueda, Macromolecules, V35, P.3104-3110, 2002.
- [12] Q.Zhang and L.A.Archer, Langmuir, V18, P.10435-10442, 2002.
- [13] X.Wang, Q.Wu, J.Dong, Y.Hu and Z.Qi, J.of Applied Polymer Science, V85, P.2913-2921, 2002.
- [14] D.Roy, A.K.Bhowmick and S.K.De, J. of Applied Polymer Science, V.49, P.263-273,1993
- [15] J.-D.Nam and J.C.Sefferis, J.of Polymer Science:Part B:Polymer Physics, V37, P.907-918, 1999.
- [16] Chia-Fen Lee, J.of Applied Polymer Science, V.88, P.312-321, 2003.
- [17] O.Meincke, B. Hoffmann, C. Dietrich, C. Friedrich, Macromolecular Chemistry and Physics, V.204, P.823-830, 2003.
- [18] A. Mousa, J. Karger-Kocsis, Macromolecular Materials and Engineering, V.286, P.260-266, 2001.
- [19] Y.T. Lim, O. O. Park, Macromolecular Rapid Communications, V.21, P.231-235, 2000.
- [20] G.Chen, S.Liu, S. Zhang, Z. Qi, Macromolecular Rapid Communications, V.21, P.746-749, 2000.
- [21] M.N.Angles, J.Salvado and A.Dufresne, J.of Applied Polymer Science, V74, P.1962-1977, 1999.
- [22] J.D. Ferry, "Viscoelastic Properties of Polymers", 3rd ed. (Wiley, New York, 1980).
- [23] G.Heinrich and M.Klüppel, Advances in Polymer Science, V160, P.1-29, 2002.
- [24] D.Pearson, L.Fetters and W.Grassley, Macromolecules, Vol.27, P.711-719, 1994.
- [25] P.R.Hornsby, Advances in Polymer Science, V139, P.1-213, 1999.



Figure 1: G* of PS280K of non-shifted and shifted data as a function of frequency



Figure 2: Shift factor vs temperature a) a_T and b) b_T .



Figure 3: Master curve of G^* of PS and PS composites vs ω at $T_0 = 160^{\circ}C$







(c) Figure 4: $G^* vs RSS wt\%$ at $T_0 = 160^{\circ}C$ and ω : a) 10^3 , b) 0.5×10^2 and c) 10^{-3} rad/s.



Figure 5: Master curve of G^{*} *of PS and PS composites vs time at T*⁰ =160°*C*



Figure 6: Master curve of J' of PS and PS composites vs ω at $T_0 = 160^{\circ}C$



Figure 7: Master curve of J" of PS and PS composites vs ω at $T_0 = 160^{\circ}C$



Figure 8: Master curve of tan δ of PS and PS composites vs ω at $T_0 = 160^{\circ}C$



Figure 9: Master curve of η^* of PS and PS composites vs ω at $T_0 = 160^{\circ}C$

www.ijeais.org