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Polystyrene Composite:
Part II: Dynamic Mechanical Characterization

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Abstract: *Residual softwood sawdust (RSS) is incorporated into polystyrene (PS). PS has sufficient high molecular weight with molecular weight 280000 g/mol. The PS composite was prepared by melt mixing technique. The dynamic mechanical tests are carried out using ARES-rheometer (Rheometric Scientific, USA) in the dynamic mode and parallel plate geometry with diameter 25 mm. The measurements were performed at temperatures ranged from 140 to 240°C and frequencies varied from 0.1 to 100 rad/s at strain 1 % and gap setting 2 mm. The dynamic mechanical properties in terms of relaxation stress modulus Gt, shear creep J(t), torque and compliance moduli for fiber –filled PS composite have been studied and compared with the original material of neat PS. The relaxation and Retardation spectra of PS composite and pure PS are evaluated.*

The results showed that the dynamic mechanical moduli are found to be improved by the incorporation of residual softwood sawdust. Therefore, Fiber-filled composites have much potential for applications of environmentally degradable plastics owing to their strength and stiffness.

Keywords: Residual softwood sawdust, polymer composite, dynamic mechanical analysis, Relaxation spectrum, Retardation spectrum

1. INTRODUCTION

Filled polymer composites are attracting ever growing interest. Therefore, a lot of research work has been carried out on reinforced polymers composites [1-14]. 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 [15] 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 [16]. 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. It is potenciated to maximize the use of renewable resources and also to minimize the wastes. So the valorization of a lignocellulosic residual material and its use as a lightweight and economical source of reinforcement in thermoplastic composites has received substantial attention [16]. Lignocellulosic materials are the most abundant renewable biomaterial of photosynthesis on earth [15]. Compared to inorganic fillers, the main advantages of lignocellulosics are their renewable nature, wide variety of fillers available throughout the world.

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 material are deformed under periodic stress [17].

The dynamic mechanical properties of polymers at small dynamic strain depend upon temperature and frequency. Dynamic mechanical analysis can be used to analyze both elastic and viscouse response simultaneously. Since most of the polymers exhibit simultaneously elastic and viscous properties and therefore are called viscoelastic [18 24].
The motivation of this work is to prepare biodegradable polystyrene composite by adding waste agricultural residues to sufficiently high commercial polystyrene and analysis this composites mechanically compared to the original material of pure polystyrene.

2. EXPERIMENTAL SECTION

- Materials and sample Preparation

In this study PS composite was prepared by adding commercial PS to residual softwood sawdust. The PS used has a sufficiently high molecular weight of 280000 g/mol (280K). The residual softwood sawdust was prepared by drying and shredding in a very small particle sizes of about 1mm. The fibers were added to the PS in 7 wt%. Composite samples were prepared by dry mixing homogenously the fiber with the polymer followed by melt mixing at about 300°C for 2 hours , then molded 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 2 mm. The samples of pure PS were press-molded also with the same dimensions of 25 mm diameter and 2 mm thickness by using press mould at about 250°C under 5 bars for about 30 minutes.

- Instrument and Measurements

The melt rheological properties of the material were determined using ARES-rheometer (Rheometric Scientifics, USA). The ARES instrument is a modular and extandable rheometer works under nitrogen atmospere in a wide range of temperatures and frequencies in the dynamic mode. In this mode of test, a sinusoidal strain is applied to a material and the resulting stress is measured by the transducer. When a sinusoidal shear stress is imposed on a linear viscoelastic polymer, the strain will also alternate sinusoidally but will be out of phase, the strain lagging the stress.

During testing at or above ambient temperature, gaseous nitrogen is used. The sample to be tested is positioned between the motor and transducer in the test station. Before placing the sample, the normal force of the system should be kept around zero. The sample is positioned on the lower plate followed by lowering the stage until the sample just contacts the upper plate completely. The actual gap size is read electronically and this allows absolute moduli to be determined. In this work the measurements were performed in the dynamic mode and 25 mm parallel plates geometry with gap settings about 2 millimeters. The soak time at the measuring temperature was 4 minutes and the strain amplitude was kept to be 1% in the whole frequency range to ensure linearity and 8 points per frequency-decade were obtained. The samples were measured in a wide range of temperature (from 140 to 240°C) as a function of frequency . The frequency ω , varied from 10^{-1} and 10^{2} rad/s. Horizontal and vertical shift factors were obtained from a two dimensional shifting.

3. RESULTS AND DISCUSSION

The log -log curves of the data measured at different temperatures were superposed into master curve at a reference temperature, T_0, by shifting in the horizontal and vertical directions as shown in Figure 1. In this Figure the shear complex modulus (G*) is plotted for un-shifted and shifted data as a function of frequency. Figure 1 shows G* decreases with increase the temperature as seen in the case of un-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 [19] as:

$$\log a_T = \log \frac{\tau(T)}{\tau(T_0)} = \frac{-c_1(T - T_0)}{c_2 + (T - T_0)} \qquad (1)$$

Where a_T is the empirically derived shift factor and constants C_1 and C_2 are material specific which are evaluated in this study for PS and PS composites and their values are listed in Table 1.

Table 1: WLF constants of PS and PS composites at T_0 = 160°C

Polymer	C_1	C_2	r^2
PS280K	6.16	94.92	0.98
PS280K/7%CF	3.46	67.77	0.72
PS280K/9%CF	6.85	172.15	0.88

The master curves of the shear compliance (the storage, $J'(\omega)$ and loss, $J''(\omega)$ compliance) for fiber-filled and unfilled PS at 160°C are logarithmically plotted against the frequency (angular) in Figures 1 and 2 . $J'(\omega)$ 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, since $\Delta E = \pi\times\sigma_0^2\times J''$ [18]. The energy loss during one cycle of strain, ΔE, is given by $\Delta E= \int\sigma d\gamma$. The stress σ depends on the maximum amplitude of stress, σo, and the phase angle, δ, between stress and strain, as $\sigma = \sigma o\times e^{i(\omega t+\delta)}$ also the strain, γ, ($\gamma = \gamma o\times e^{i\omega t}$) correlates to the maximum amplitude of strain, γo, and the frequency, ω. Therefore, if γo is kept constant during dynamic deformation (corresponding to constant strain, constant stress, or constant energy input), the energy loss is proportional to J''. When a sinusoidal strain is imposed on a linear viscoelastic material, a sinusoidal stress response will result and the dynamic mechanical properties depend only upon temperature and frequency, independent of the type of deformation (constant strain, constant stress, or constant energy).

Figures 1-2 represent three distinct regions of behavior and that is typically for flexible-chain monodisperse homopolymer as, the glass transition, rubbery plateau, and terminal zones.

The incorporation of RSS into PS results in enhancing the shear compliance as shown in Figures1-2. As an example in Figure 1 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 because of the formation of the network, hence the increase in the strength of the PS/RSS composite.

The torque is investigated for the samples of pure PS and PS composite and logarithmically plotted as a function of the frequency as shown in Figure 3. In this Figure the torque increases monotonically by many orders of magnitude with increasing ω up to about 4 radian/s then increases gradually. And the value of the torque for PS composite is higher than this of pure PS. As shown in Figure 3, at 100 radian/s the torque increased from 4.7×10^{-3} to 7×10^{-3} NM. This because of the increase in the strength and stiffness of the PS by the addition of the RSS since the formation of a polymer matrix-fibers network consisted of polymer chains and fibers.

The shear relaxation modulus G(t) for fiber-filled and unfilled PS is plotted against time with logarithmic scales in Figure 4. The modulus G(t) defined as the relaxation stress/strain ratio at constant deformation. At intermediate times G(t) flattens somewhat at a level which is associated with the average spacing between entanglement coupling points. The height of G (t) at the intermediate time (rubbery zone) is the plateau modulus, G_N^o . In this study G_N^o was evaluated from the rubbery zone in G(t) to be about 0.23 and 0.18 MPa for 7% fiber filled-PS and unfilled PS, respectively as shown in figure 4. Generally Figure 4 shows higher G(t) for fiber-filled samples than this in the cases of unfilled sample. This again evidence for the high stiffness and strength of composites compared to pure PS. The width of the rubber-like regime for PS composite is observed to be longer than this of pure PS. May be because of the formation of the temporary entanglements between the cellulosic fiber and the polymer chains and that is proved too at the longest relaxation time. At long times G(t) falls sharply and approaches the longest relaxation time, τ_d .τ_d is defined as, the time required to leave the chain completely its tube (the constraint of their surrounding chains) by reptation or snake- like motion. τ_d is enlarged for fiber-filled PS, since it increases from around 1.1 second to 4 seconds by the addition of 7% filler as shown in Figure 4. That is due to the resistance of the fiber for the mobility of the chain due to the formation of the temporary entanglements. Therefore the time needed for the chains to move within the constraint of their surrounding molecules is long.

The observations in Fig. 4 are found for the shear creep stress, J(t) in Figure 5. Since the logarithmic plots of J(t) have roughly the appearance of mirror image of G(t) plot reflected in the time axis. In Figure 5 J(t) for pure PS and 7% fiber-filled PS are plotted as a function of time. This Figure indicates that J(t) increases with time and the effect of the RSS addition is clear since values of J(t) at 0.1 second are 1.14×10^{-5} and 7.94×10^{-6} Pa^{-1} for filled and unfilled PS, respectively. As explained above due to the networks formation.

The relaxation spectrum H (Fig 6) and retardation spectrum L (Fig 7) are logarithmically plotted versus time. They refer to the deformation in shear . Besides, they are useful qualitatively in gauging the distribution of relaxation and retardation mechanisms, respectively in different regions of the time scale. In real polymers a broad spectrum of relaxation times exists due to the huge freedom of polymer chain configurations. These Figures indicate the effect of the addition of fiber to the PS, since the increase in the strength and stiffness of PS by the addition of RSS reflects in relaxation and retardation spectrum as shown in Figures 6-7 . Since at 0.01 second H(t) increases from about 1.6×10^{4} to 3.7×10^{4} Pa and L(t) changes from 1×10^{-6} to 2×10^{-6} Pa^{-1} by the incorporation of 7% filler to the sufficiently high molecular weight PS.

4. CONCLUSION

In this study PS composites are prepared by melt-mixing technique for residual softwood sawdust with PS has molecular weight 280000 g/mol. The waste agricultural residue is dried and shredded in a fine particles. The samples of pure PS and PS composites were melded for the dynamic mechanical measurements under press-mould in a disc form with 25 mm diameter and 2 mm thickness.The dynamic mechanical measurements are 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 2 mm. The dynamic mechanical properties in terms of relaxation stress modulus Gt, shear creep J(t) , torque, and compliance moduli of PS composite have been studied and compared with the original material of pure PS. The dynamic mechanical properties are found to be improved by the addition of RSS and their values rise with filler loading. Therefore, Fiber-filled composites have much potential for applications of environmentally degradable plastics owing to their strength and stiffness.

5. ACKNOWLEDGMENTS

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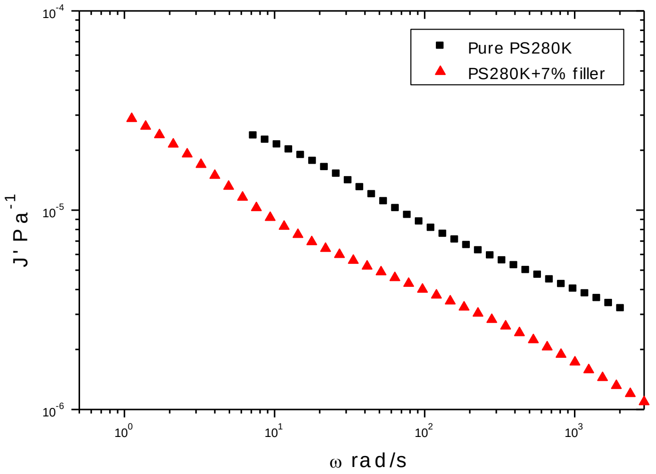

Figure 1: Master curve of J' for filled and unfilled PS280K vs ω at T_0 =160°C

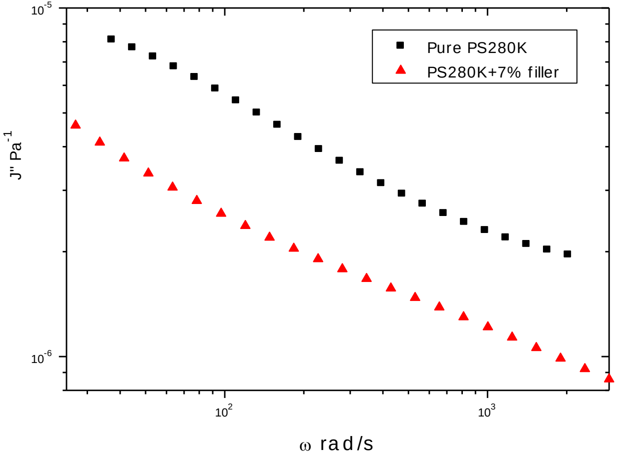

Figure 2: Master curve of J" for filled and unfilled PS280K vs ω at T_0 =160°C

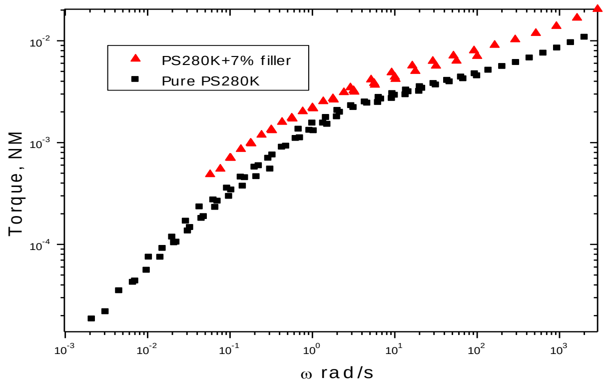

Figure 3: Master curve of the torque for filled and unfilled PS280K vs ω at T_0 =160°C

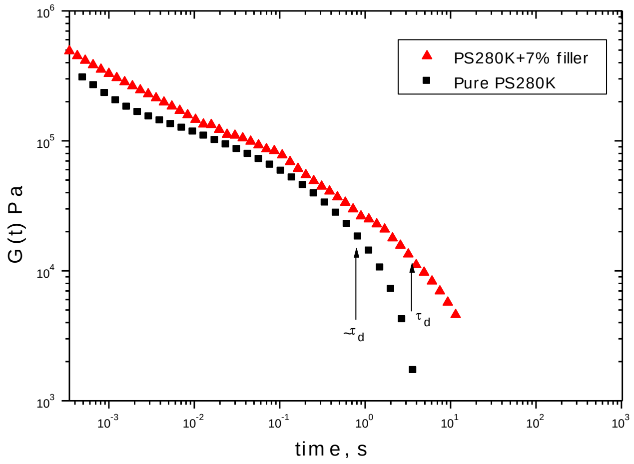

Figure 4: Master curve of G(t) for filled and unfilled PS280K vs time at T_0 =160°C

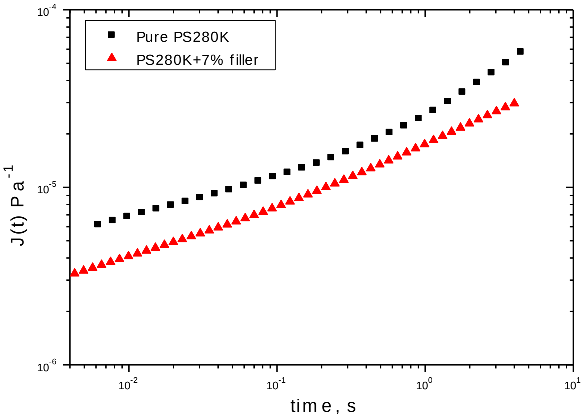

Figure 5: Master curve of J(t) for filled and unfilled PS280K vs time at T_0 =160°C

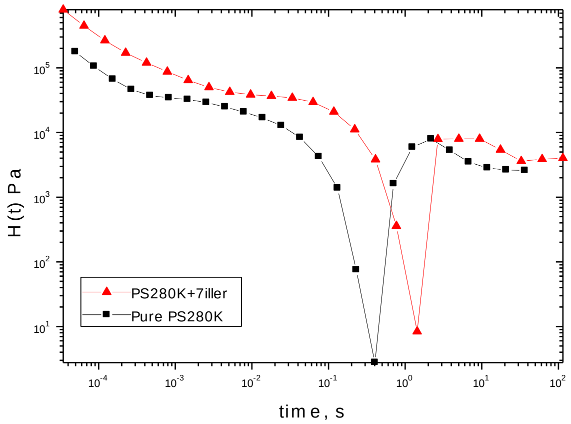

Figure 6: Master curve of H(t) for filled and unfilled PS280K vs time at T_0 =160°C

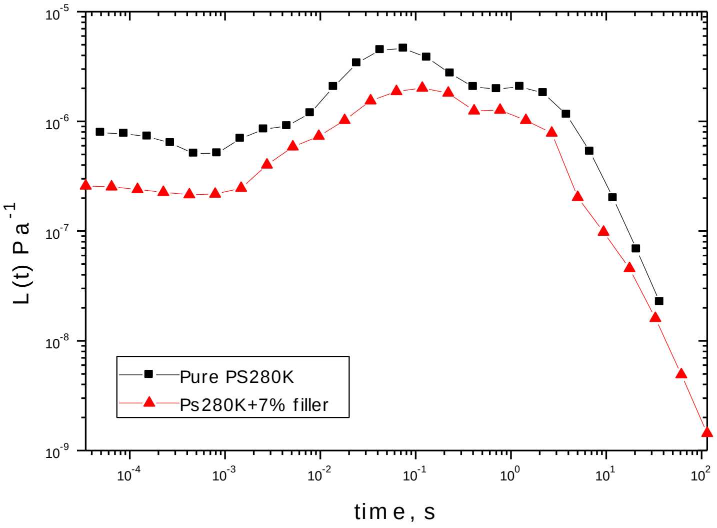

Figure 7: Master curve of L(t) for filled and unfilled PS280K vs time at $T_0 = 160°C$