

# Complex Modulus of Waste Tires Reinforced Polystyrene

Mahmoud Abdel-Halim Abdel-Goad

Chemical Engineering Dept., Faculty of Engineering, Minia University, Egypt  
(E-mail:m.abdelhalim@mu.edu.eg)

**Abstract:** In this work, polystyrene/waste tires composites were prepared by incorporating of waste tires into polydisperse commercial polystyrene in a melt-mixing method. The rheological characterization of PS and PS/composite have been studied and compared. These properties were studied using ARES-Rheometer under nitrogen atmosphere in parallel plate geometry with diameter 8 mm. The measurements are carried out over a wide range of temperatures ranged from 120°C to 220°C and frequencies from 100 to 0.1 radians per second. The complex modulus ( $G^*$ ) were evaluated and compared with those of unfilled PS. The dynamic mechanical properties and stability at elevated temperatures were found to increase with the addition of waste tires to PS as confirmed by the results.

The results showed that the value of  $G^*$  at  $\omega = 1.0$  radian/s is  $1.8 \times 10^4$  and  $4.4 \times 10^4$  Pa for PS and PS/waste tires, respectively. This difference rises at low frequencies-branch to be the value of  $G^*$  at  $\omega = 0.06$  radian/s is  $8.8 \times 10^2$  and  $7.8 \times 10^3$  Pa for PS and PS/waste tires, respectively. Generally  $G^*$  increases by the addition of rubber as filler for PS

**Keywords:** Polystyrene/waste tires composite, Rheology, Complex modulus

## 1. INTRODUCTION

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 optimised to utilize all potentials of particulate filling. Optimization must include all aspects of the composites from component properties, through structure and especially interactions [1].

Disposal of waste rubber material is a global problem, and used tires constitute the largest volume of scrap rubber. Recycling of waste tires is essential due to economic and environmental reasons. Utilization of ground waste rubber has been reviewed recently. Finely ground waste tire rubber has been used as filler in rubbers and in thermoplastics [2]. Physical properties and processability are reported to be adversely affected when large volumes of waste rubber is added to a rubber compound.

Dynamic mechanical analysis over a wide range of temperature and frequencies permits the determination of the viscoelastic behavior of molten polymers and, in particular, the study the glass transition of reinforced composites. Therefore, the investigations of the polymer composites using the mechanical and the dynamic mechanical analysis are becoming of great interesting [3-18].

The purpose of this work was to characterize in details the complex modulus of rubber filled polystyrene compared to the original material of unfilled polystyrene.

## 2. EXPERIMENTAL SECTION

### Samples preparation and characterization

PS/waste tires composite was prepared by introducing waste tires into commercial PS with molecular weight about  $2 \times 10^7$  g/mol. The waste tires were shredded into small particles sizes of about 2 mm. The mixture of PS and 12 wt % shredded tires are dry mixed by hand-mixing for around half an hour and heated at 300°C for 2 hours. Followed by preparation the samples of filled and unfilled PS for the rheological measurements under compression-mold at 190°C for 3 hours and 15 bars in a disc form with diameter 8 mm and thickness 2.2 mm.

## 3. MEASUREMENTS

The dynamic mechanical measurements were performed for PS and PS composite by using an ARES-Rheometer (Rheometric Scientific). The rheometer was operated in the dynamic mode on the plate-plate geometry of 8mm diameter and about 2 mm gap. The gap size changes with the temperatures and is read electronically and allows absolute moduli to be determined. The measurements were performed in this study for the samples under nitrogen atmosphere, strain amplitude 1%, over temperature ranged from 120 to 220°C and angular frequency ( $\omega$ ) varied from  $10^2$  to  $10^{-1}$  radian/s.

#### 4. RESULTS AND DISCUSSION

In this study the experiments data which measured over a wide range of the temperature are shifted into a single log -log curve at a reference temperature  $T_0$  by using of the time-temperature superposition principle which described by Williams-Landel-Ferry [19] as,  $\log a_T = -C_1 (T-T_0) / (C_2 + (T-T_0))$ . Where  $a_T$  is the horizontal shift factor and constants  $C_1$  and  $C_2$  are material specific.  $a_T$  shifts the data obtained at different temperatures along the log frequency,  $\omega$  axis as shown in Fig.1 and in vertical direction is given purely by  $b_T$  ( $b_T = \rho T / \rho_0 T_0$  [20]). Where  $\rho$  is the material density.

Figure 1 shows the shear complex modulus ( $G^*$ ) as a function of frequency at temperatures ranged from 120 to 220°C. By choosing the reference temperature at 180°C, the horizontal shift factor shifts the high temperatures data of  $G^*$  toward right side at low frequencies-branch along of  $G^*$  which measured at 180°C and those at the low temperatures are shifted at high frequencies-branch as shown in Figure 1. The vertical shift factor rises  $G^*$  of the high temperatures to  $G^*$  of 180°C and decreases those at low temperatures to reach  $G^*$  of 180°C as shown in Figure 3. Because  $G^*$  modulus decreases with increasing the temperatures as it is clear from Fig.1.

The master curves of the shear complex modulus,  $G^*$  for PS and PS/waste tires at 180°C are logarithmically plotted against the angular frequency as seen in Figure 2. This quantity of  $G^*$  is a combination of the storage modulus ( $G'$ ) and loss modulus ( $G''$ ) as,  $G^* = G' + i G''$  [21].

Where,  $G'$  is the ability of the material to store energy in the cycle of the deformation and  $G''$  is the energy dissipated as heat in this cycle. Master curves of  $G^*$  for PS and PS/waste tires display three distinct regions of behavior and that is typically for flexible-chain monodisperse homopolymer. These region are : the dynamic glass transition, rubbery plateau, and flow zones from the right side to the left side. At the flow regime,  $G^*$  decreases further as shown in Figure 2. This corresponding to the complete relaxation of polymer chains at low shear rate, where the time allowed for relaxation is longer than the longest relaxation time in the polymer. The dynamic glass transition zone is located at high frequencies at which the shear rate is higher than the average relaxation time of the polymer chain. Therefore, the chains can not adjust quickly enough to dissipate the applied stress as a result, the observed modulus is high. As the deformation shear rate decreases,  $G^*$  decreases until the intermediate regime of a rubber-like plateau is observed. This rubber-like region is somewhat flat and it is nearly independent on the frequency over the frequency range from about  $1 \times 10^3$  to 10 radians/s as shown in Figure 2. This rubber like behavior reflects the elasticity of the polymer and it is due to the entanglement of the chains, this entanglement depends on the type and the long of the chains. From the beginning of this regime of the rubber-like,  $G^*$  is observed to rise for PS/waste tires composite than this of the original PS and this increase is significantly continued over the flow regime too at low frequencies as shown in Figure 2. As an example, the value of  $G^*$  at  $\omega = 1.0$  radian/s is  $1.8 \times 10^4$  and  $4.4 \times 10^4$  Pa for PS and PS/waste tires, respectively. But this difference rises at low frequencies-branch to be the value of  $G^*$  at  $\omega = 0.06$  radian/s is  $8.8 \times 10^2$  and  $7.8 \times 10^3$  Pa for PS and PS/waste tires, respectively. Generally this increase in  $G^*$  by the addition of rubber as filler for PS is may be because the interaction between the rubber particles and the PS chains which increases the stiffness of the chains. The significant increase at low frequencies (means at long time and high temperature) may be due to the formation of the rubber-PS network. Since the formation of this matrix increases with the time at high temperature.

#### 5. CONCLUSION

In this study the PS/waste tires composite were prepared. The Rheological properties for PS composite are evaluated and compared to those of the original material of unfilled PS. These properties are determined by ARES Rheometer under nitrogen atmosphere in parallel plate geometry with diameter 8 mm. The measurements are carried out over a wide range of temperatures, ranged from 120°C to 220°C and frequencies from 100 to 0.1 radians per second.

The results showed that the value of  $G^*$  at  $\omega = 1.0$  radian/s is  $1.8 \times 10^4$  and  $4.4 \times 10^4$  Pa for PS and PS/waste tires, respectively. This difference rises at low frequencies-branch to be the value of  $G^*$  at  $\omega = 0.06$  radian/s is  $8.8 \times 10^2$  and  $7.8 \times 10^3$  Pa for PS and PS/waste tires, respectively. Generally  $G^*$  increases by the addition of rubber as filler for PS

#### 6. ACKNOWLEDGMENTS

The financial support by the International Bureau in Germany, helpful discussions of Dr. W.Pyckhout –Hintzen at research center Juelich, Germany are greatly acknowledged.

## REFERENCES

- [1]. B.Pukanszky, E.Fekete, “Adhesion and surface modification”, Advances in Polymer Science, V139, P.110-153, Springer-Verlag Berlin Heidelberg, 1999.
- [2]. J. I. Kim , S. H. Ryu , Y. W. Chang, “Mechanical and dynamic mechanical properties of waste rubber powder/HDPE composite”, J. of Applied Polymer Science, V.77, P. 2595-2602, 2000.
- [3]. W.Guo, M.Ashida, “**Dynamic viscoelasticities for short fiber-thermoplastic elastomer composites**”, J. of Applied Polymer Science, V50, P.1435-1443, 1993 .
- [4]. P. K. Sengupta, D. Mukhopadhyay ,”**A dynamic mechanical study on unidirectional carbon fiber-reinforced polypropylene composites**” J.of Applied Polymer Science, V51, P.831-840, 1994
- [5]. G. Kalaprasad, G. Mathew, C. Pavithran, S. Thomas , “**Melt rheological behavior of intimately mixed short sisal-glass hybrid fiber-reinforced low-density polyethylene composites. I. Untreated fibers**”, J. of Applied Polymer Science, V89, P.432-442, 2003
- [6]. L. Ibarra, A. Macías, E. Palma , “**Viscoelastic properties of short carbon fiber thermoplastic (SBS) elastomer composites**”, J.of Applied Polymer Science V57, P.831-842, 1995
- [7]. P. V. Joseph, G. Mathew, K. Joseph, S. Thomas, P. Pradeep,” **Mechanical properties of short sisal fiber-reinforced polypropylene composites: Comparison of experimental data with theoretical predictions**”, J.of Applied Polymer Science, V88, P.602-611, 2003
- [8]. V. M. Murty, S. K. De, S. S. Bhagawan, R. Sivaramakrishnan, S. K. Athithan, “**Viscoelastic properties of short-fiber-reinforced rubber composites and the role of adhesion**”, J.of Applied Polymer Science, V28, P.3485-3495, 1983
- [9]. D. Roy, A. K. Bhowmick, S. K. De, “**Dynamic mechanical properties of short carbon fiber-filled styrene-isoprene-styrene block copolymer**”, J.of Applied Polymer Science, V49, P.263-273, 1993
- [10]. S.Yano, S. Hirose, H. Hatakeyama, B. Westerlind, M.Rigdahl, “**Dynamic viscoelasticity of isoprene rubber reinforced with short cellulose fibers**” J.of Applied Polymer Science, V40, P.657-667, 1990
- [11]. G. Kalaprasad, S. Thomas, “**Melt rheological behavior of intimately mixed short sisal-glass hybrid fiber-reinforced low-density polyethylene composites. II. Chemical modification**”, J.of Applied Polymer Science, V89, P.443-450, 2003
- [12]. Xiaoyi Gong , “**The dynamic mechanical behavior of random-in-plane short fiber-reinforced epoxy resin composites**”, Polymers for Advanced Technologies, V7, P.141-145, 1996
- [13]. L.Ibarra, C.Chamorro , “**Short fiber-elastomer composites. Effects of matrix and fiber level on swelling and mechanical and dynamic properties**”, J.of Applied Polymer Science, V43, P.1805-1819, 1991
- [14]. Michio Ashida, Toru Noguchi, Satoshi Mashimo, “**Effect of matrix's type on the dynamic properties for short fiber-elastomer composite**”, J.of Applied Polymer Science, V30, P.1011-1021, 1985
- [15]. L.I.Rueda, C.C. Antón, M. C. Rodríguez, “**Viscoelastic properties of short fiber filled SBR composites**”, Angewandte Makromolekulare Chemie, V160, P.29-39, 1988
- [16]. L. Ibarra, “ **Dynamic properties of short fiber-EPDM matrix composites as a function of strain amplitude**”, J.of Applied Polymer Science, V54, P.1721-1730, 1994
- [17]. M. Ashida, T. Noguchi, S. Mashimo, “**Dynamic moduli for short fiber-CR composites**”, J.of Applied Polymer Science, V29, P.661-670, 1984
- [18]. A. K. Rana, B. C. Mitra, A. N. Banerjee, “**Short jute fiber-reinforced polypropylene composites: Dynamic mechanical study**” J.of Applied Polymer Science, V71, P.531-539, 1999
- [19]. J.D. Ferry, “Viscoelastic Properties of Polymers”, 3rd ed. ( Wiley, New York, 1980)
- [20]. Mahmoud A.-Halim Abdel-Goad, “Synthesis Characterization, Rheological Properties and Microscopic Dynamic of Polymers with low Plateau Moduli” Phd’s thesis, Muenster University, Germany, 2000.
- [21]. G.Heinrich, M.Klueppel, “Recent advances in the theory of filler networking in elastomers”, Advances in Polymer Sciences, V160, P.1-44, Springer-Verlag Berlin Heidelberg, 2002.

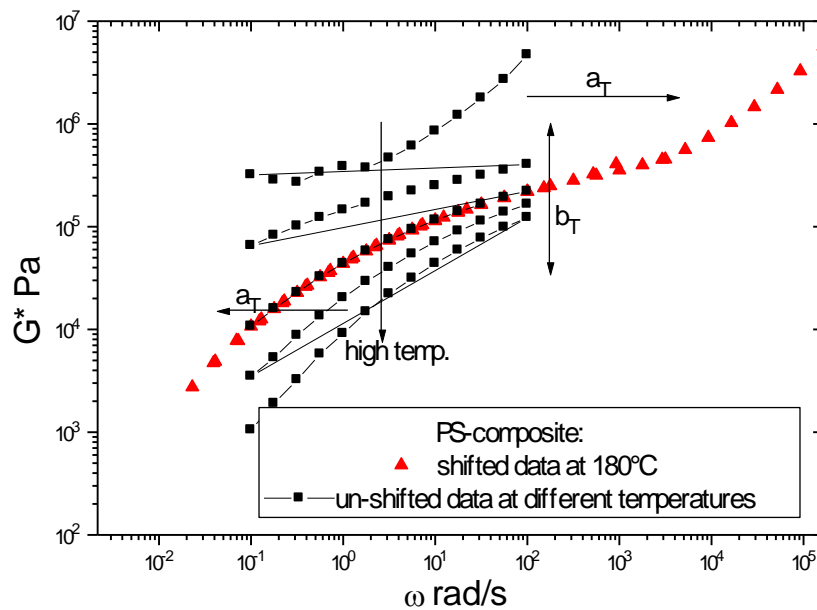


Figure 1: Experiments data of  $G^*$  were measured at different temperature as a function of  $\omega$  for PS and PS composite and shifted at  $T_0 = 180^\circ\text{C}$  by using  $a_T$  and  $b_T$ .

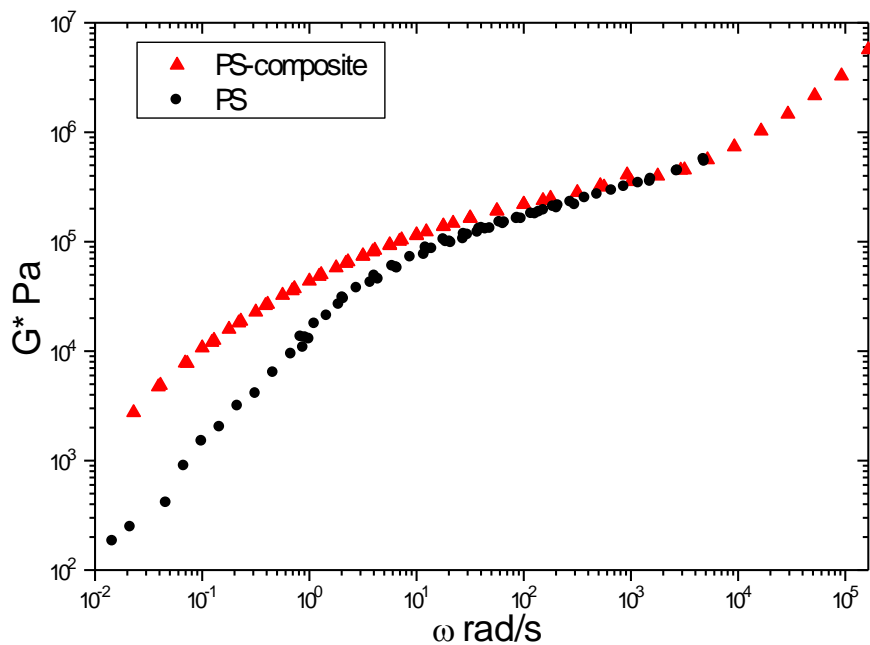


Figure 2: Master curve of  $G^*$  as a function of  $\omega$  for PS and PS composite at  $T_0 = 180^\circ\text{C}$ .