# Effect of polymer processing and environmental factors on molecular weight and thermal properties of polystyrene

M Saiful Islam<sup>\*</sup>, Swapan K Ray, M Amirul Hoque, Shahin Sultana and Husna P Nur BCSIR Laboratories, Dhaka, Dhanmondi, Dhaka-1205, Bangladesh.

### Abstract

The effect of polymer processing operation as well as the environmental factors- soil, water, air and light on molecular weight and thermal properties of polystyrene (PS) was studied. The virgin PS pellet was firstly compression molded to transparent sheet at 250 <sup>o</sup>C and at 200 KN pressure without any additives. Samples of the molded sheets were placed in an open environment, in contact with soil, water, air and light for the time period of six (06) months. At the same time control PS sheet samples were placed in a closed container and in dark place for the similar period of time. All the samples were then examined with gel permeation chromatography (GPC) for average molecular weight (Mw) and molecular weight distribution. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of all the samples were also studied in a simultaneous thermal analyzer (STA). The change in average molecular weight (Mw), molecular weight distribution and thermal properties, such as, glass transition temperature (Tg), crystalline melting temperature, decomposition temperature and residue after heating were studied and found quite insignificant change in most of the properties of PS samples. Thus there is a good prospect to recycle and reuse PS sheet waste like its original virgin resin applications.

**Keywords:** Polystyrene; processing; weathering; molecular weight; thermal properties; reusability.

### **1. Introduction**

Polystyrene (PS) is one of the mostly used synthetic polymer in the daily necessaries and in the packaging industries. In many cases after using as packaging purpose the PS sheets are kept in open place for long period of time or burnt it out. The management of this huge polymer waste in environmental friendly way is truly a difficult task. As a non biodegradable polymer, a way to manage this problem is to reuse it. But, whether any change in molecular weight and thermal properties occurred due to the processing operation and environmental factors needs to be studied. Envisaging the prospect of reuse of polystyrene waste, this study has been conducted. A number of studies in the similar area have been conducted earlier. Effects of extrusion on the structure and properties of high-impact polystyrene was studied by Kalfoglou and Chaffey (2004) and found good properties retained after normal processing. Photodegradation and photostabilization of polymers, especially polystyrene were studied by Yousif and Haddad (2013). Zahra and Shenta (2009) investigated the photostabilization of polystyrene films by anthraquinones derivatives and their complexes with copper (II), oxovanadium (IV) and nickel (II) ions. Aliwi et al (2001) studied photostabilization of polystyrene films by Nickel and Copper tetradentate Shiff base complexes. Pinto et al (2013) studied photodegradation of polystyrene films containing UV-visible sensitizers. Ruoko (2012) studied UV light induced degradation of polyethylene and polystyrene – spectroscopic and DSC study. Eldin and El-laithy (1994) studied photooxidative degradation of polystyrene of cover signals lamp of some automobile. Weir (1998) investigated the new aspect of photodegradation and photooxidation of polystyrene. The effects of processing and using different types of clay on the mechanical, thermal and rheological properties of high-impact polystyrene nanocomposites, was studied by Isfahani et al (2013). Stromberg et al (2005) studied the identifying the opportunities for plastics recovery. Scaffaro and Mantia (2002) studied virgin/recycled homopolymer blends. Mantia et al (2002) investigated the reprocessing behaviour of recycled plastics. Thermophysical and mechanical properties of polystyrene: influence of free quenching was studied by Rouabah et al (2012). Rouabah et al (2008) also studied the mechanical and thermal properties of polycarbonate: influence of free quenching. Kashiwagi et al (1995) studied the thermal and oxidative degradation of poly (methyl methacrylate), molecular weight. Hirata et al (1995) studied the thermal and oxidative degradation of poly (methyl methacrylate), weight loss. Kashiwagi et al (1996) also studied the effect of weak linkages on the thermal and oxidative degradation of poly (methyl

methacrylate). Kashiwagi and Inabi (1996) studied the behavior of primary radicals during thermal degradation of poly (methyl methacrylate). Brauman (1998) studied polymer degradation during combustion. Gijsman et al (1993) studied the mechanism of the Low-Temperature oxidation of polypropylene. Hirschler (1982) studied the effect of oxygen on the thermal decomposition of poly (vinyl fluoride). Inabi and Kashiwagi (1997) examined a calculation of thermal degradation initiated by random scission, unsteady radical concentration. Kashiwagi and Nambu (1992) studied the global kinetic constants for thermal oxidative degradation of a cellulose paper. Molecular weight distributions of linear polymers: detailed analysis from GPC studied by Kissin (1995). Kinetics of the thermal and thermooxidative degradation of polystyrene, polyethylene and poly (propylene) was studied by Jeffery et al (2001). Schnabel (1991) studied the polymer degradation: principles and practical applications. Degradation and stabilization of polymers: theory and practice was studied by Zaikov (1995). The thermal properties and molecular weight of a synthetic polymer resin are very important factors for its applications as well as its recyclability. The objective of this study was to investigate the influence of polystyrene processing operation and the effect of various environmental factors on changing the molecular weight and thermal properties to check the reusability of the recycled PS.

### 2. Materials and Methods

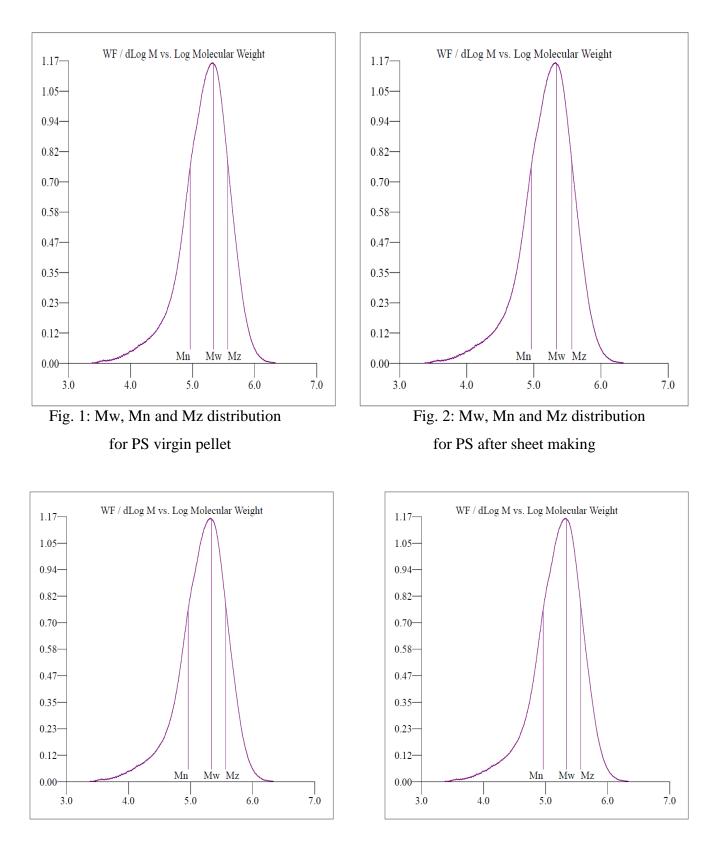
Laboratory reagent grade polystyrene pellet resin was purchased from BDH Chemicals ltd., England with average molecular weight (Mw) of 1,00,000. A weber pressen brand compression molding machine of Germany was used to make PS molded transparent sheet. A temperature of 250°C (10 °C above the melting point of PS) and pressure 200 kilonewton (KN) were used with water circulating cooling system. Five samples were placed in a designated open place with the contact of soil, water, air and light. Five control samples were placed in closed container in the dark place of the laboratory. After six month, all the samples along with the virgin pellet resin were taken into the analytical experimental section. Virgin resin and all the samples under investigation were analyzed with Malvern-Viscotek-TDA GPC instrument for average molecular weight (Mw) and molecular weight distribution. The solvent for GPC analysis was tetrahydrofuran (THF) with flow rate 1.0 ml/min and the oven temperature was  $30^{\circ}$ C. The injection volume was 100 µL and the run time was 40 min for each sample. TGA and DTA of all the samples were performed in a STA instrument of STA

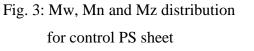
449 F3, NETZSCH, Germany. The heating rate of STA analysis was 20 °C/min from 25 °C up to 900 °C and nitrogen gas was purged to maintain inert atmosphere. The PS samples were taken about 20-30 mg in each case and alumina crucible was used in the steel furnace of STA instrument.

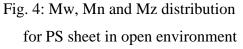
## 3. Results and Discussion

3.1. Molecular weight (Mw) and molecular weight distribution: The GPC results showed the molecular weight of the virgin PS resin was 1,05,844 daltons. Molecular weight distribution or polydispersity index (Mw/Mn) was found to be 2.175. For PS immediately after processing the average molecular weight value was 1,04,910 daltons and Mw/Mn was 2.391. For control sample the average molecular weight (Mw) value was 1,04,866 daltons and Mw/Mn was 2.393. For the sample exposed to the environment, the average molecular weight value was 1,04,036 daltons and Mw/Mn was 2.426. The molecular weight distribution curves (WF/dLogm vs. Log Molecular Weight) are shown in Figure 1, 2, 3 and 4 for virgin PS pellet, for PS molded sheet immediately after processing, for PS sheet at control and PS sheet at open environment respectively.

The average molecular weight (Mw) and the molecular weight distribution or polydispersity index (Mw/Mn) was found almost similar for each case which is depicted in the figures. Thus the polymer processing and environmental factors have little effect on the molecular weight (Mw) and the molecular weight distribution of PS.







3.2. Thermal analysis by STA: All the samples were analyzed by simultaneous thermal analyzer (STA) for obtaining the TGA and DSC curves. The graphs are shown for PS pellet, PS sheet immediately after molding, PS sheet control sample and PS sheet at open environment in the figure 5, 6, 7 and 8 respectively. From the graphs it was found that the glass transition temperature of the virgin PS pellet was 94.1 <sup>o</sup>C, for PS sheet immediately after molding was 98.1 <sup>o</sup>C, for PS sheet at control condition was 99.2<sup>o</sup>C and for PS sheet at open environment was 99.6 <sup>o</sup>C. The glass transition temperature shows increasing trend but the changes were not significant. The melting temperature were for the same were found to be 172.1 <sup>o</sup>C, 155.3 <sup>o</sup>C, 155.3 <sup>o</sup>C and 161.8 <sup>o</sup>C. In this case the melting points were lower but still not significant. A slight decreasing of melting point might be for some degradation during processing and by environmental factors and the decrease in molecular weight which are found from the molecular weight analysis by GPC.

The degradation temperature for PS virgin pellet was 435.4 <sup>o</sup>C and for all the other three cases the value were about 438 <sup>o</sup>C. The increasing trends were observed in this case. The degradation for all cases were near about 98-99% of its initial mass. The residues on heating were also in between 0.8 to 1.5 % and no significant change/ increase were observed for processing or for the environmental factors. Thus the polymer processing operation and environmental factors such as soil, water air and light have very little effect on thermal properties. So, the recycle and reuse of the PS might be possible almost in the same level of applications like virgin PS resin.

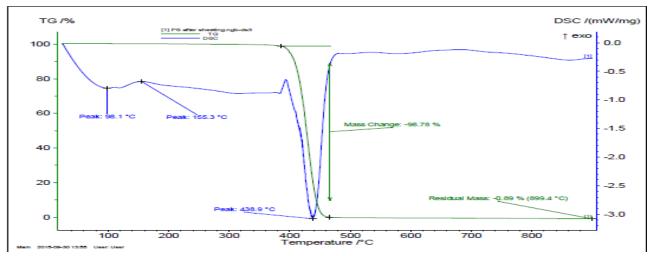


Fig. 7: TGA-DSC curve for PS sheet immediately after molding

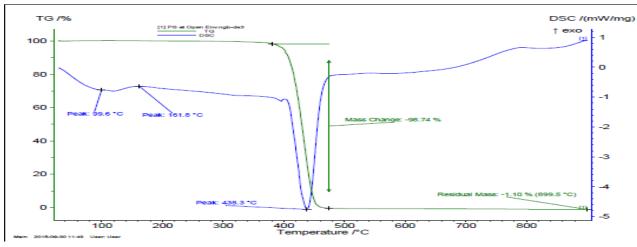


Fig. 8: TGA-DSC curve for PS sheet at open environment after six month

#### 4. Conclusion

The effect of polymer processing operation on molecular weight (Mw), molecular weight distribution and thermal properties was investigated and found nominal difference. Though some change observed but the effect was found to be insignificant. The Mw values were about 1,00,00 daltons and the molecular weight distribution were slightly above 2 for each case. The environmental factors- soil, water air and light also produced small change in molecular weight (Mw), molecular weight distribution and thermal properties. The glass transition temperatures (Tg), melting points and decomposition temperatures were almost identical to virgin PS pellet. The weight losses found from TGA curve were also very much similar. The residues on heating were very small for all the experiments and were almost same. Thus from this study it might be concluded that most of the properties of PS resin retain to its original state avoiding the processing operation effect and all the environmental factors. So it was found that PS maintains its recyclability and reusability almost in similar level of virgin PS resin.

### References

Aliwi, S.M., AL-Ani, R.R. and Awad, D.A.J., (2001), Photostabilization of polystyrene films by Nickel and Copper tetradentate Shiff base complexe, Iraqi journal polymer, 5(1): 15-30.

Brauman, S.K., (1998), Polymer degradation during combustion, J. Polymer Sci., B, 26, pp. 1159-71.

Eldin, N.M. S. and El-laithy, S.A., (1994), Photooxidative degradation of polystyrene of cover signals lamp of some automobile. Journal of applied polymer science. 55:47–54.

Gijsman, P., Hennekens, J. and Vincent, J., (1993), The mechanism of the Low-Temperature oxidation of polypropylene, polymer degradation and stability, 42, pp. 95-105.

Hirata, T., Kashiwagi, T. and Brown J.E., (1995), Thermal and oxidative degradation of Poly (methyl methacrylate), Weight loss, Macromolecules, 18, pp. 1410-1418.

Hirschler, M.M., (1982), Effect of Oxygen on the Thermal decomposition of poly (vinyl fluoride), Europ. Polymer J. 18, pp. 463-67.

Inabi A. and Kashiwagi, T., A (1997), calculation of Thermal degradation initiated by random scission, unsteady radical concentration, Eur. Polym. J. 23, 11, pp. 871-881.

Isfahani, A. P., Mehrabzadeh, M. and Morshedian, J., (2013), The effects of processing and using different types of clay on the mechanical, thermal and rheological properties of highimpact polystyrene nanocomposites, Polymer Journal 45, 346-353.

Jeffery, D., Peterson, S. Vyazovkin, A. and Wight, C., (2001), Kinetics of the Thermal and Thermo-Oxidative Degradation of Polystyrene, Polyethylene and Poly(propylene), Macromolecular Chemistry and Physics.

Kalfoglou N. K. and Chaffey, C. E. (2004), Effects of extrusion on the structure and properties of high-impact polystyrene, Engineering & Science, Volume 19, Issue 8, pages 552-557.

Kashiwagi, T., Inabi, A., Brown, J., Hatada, E K., Kitayama, T. and Masuda, E., (1996), Effect of weak linkages on the thermal and oxidative degradation of Poly (methyl methacrylate), Macromolecules, 19, pp. 2160-2168.

Kashiwagi, T. Hirata, T. and Brown, J.E., (1995), Thermal and oxidative degradation of Poly (methyl methacrylate), Molecular weight, Macromolecules, 18, pp. 131-138.

Kashiwagi, T. and Inabi, A., (1999), Behavior of primary radicals during thermal degradation of Poly (methyl methacrylate), Polymer Degradation and Stability, 26, pp. 161-184.

Kashiwagi, T. and Nambu, H., (1992), Global kinetic constants for thermal oxidative degradation of a cellulose paper, Combust. Flame, 88, pp. 345-68.

Kissin, Y. V., (1995), Molecular weight distributions of linear polymers: Detailed analysis from GPC, Journal of polmer science part A: 30.

La Mantia, F. P., Gaztelumendi, M. Eguiaza'bal, J. I. and Naza'bal, J. (2002), 'Properties -Reprocessing Behaviour of Recycled Plastics', Rapra Technology Limited, Shawbury.

Pinto, L., Goi, B., Schmitt, C. and Neumann, M., (2013), Photodegradation of polystyrene films containing UV-visible sensitizers, Journal of Research Updates in Polymer Science. 2:39–47.

Rouabah, F. Fois, M. and Ibos, L., (2008), "Mechanical and thermal properties of polycarbonate, part 1: influence of free quenching," Journal of Applied Polymer Science, vol. 109, no. 3, pp. 1505–1514.

Rouabah, F., Dadache, D. and N. Haddaoui, (2012), Thermo-physical and Mechanical Properties of Polystyrene: Influence of Free Quenching, ISRN Polymer Science.

Ruoko, (2012), UV light induced degradation of polyethylene and polystyrene – spectroscopic and DSC study. Msc thesis: Tampere University of Technology.

Scaffaro, R., La Mantia, F. P., (2002), "Virgin/Recycled Homopolymer Blends", Rapra Technology Limitedm, Shawbury.

Schnabel, W., (1991), "Polymer Degradation: Principles and Practical Applications", Macmillan, New York.

Stromberg, E., Vilaplana, F., Agren, S., Ribes-Greus, A. and Karlsson, S., (2005), Identifying the Opportunities for Plastics Recovery, Brussels, Conference Proceedings.

Weir, N.A., (1998), New aspect of photodegradation and photooxidation of polystyrene. Europ Polym J. 14:9–14.

Yousif E. and Haddad, R., (2013), Photodegradation and photostabilization of polymers, especially polystyrene: review, Springerplus, 2: 398.

Zahra M.A.A. and Shenta, A.A., (2009), Photostabilization of polystyrene films by anthraquinones derivatives and their complexes with copper (II), oxovanadium (IV) and nickel (II) ions, Journal of Basrah Researches. 35(3):81–97.

Zaikov G. E., (1995), "Degradation and Stabilization of Polymers: Theory and Practice", Nova Science Publishers, Commack, New York.