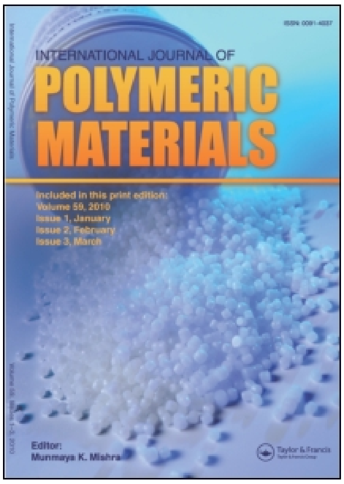

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Characterization of Some Post-Consumer Thermoplastic Food Packaging Reclaimed from Remote Desert Areas in Saudi Arabia

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Discarded plastic food packaging articles taken from the Thomamah desert area near Riyadh in Saudi Arabia were characterized rheologically and thermally. These articles are made of polystyrene (PS), high-density polyethylene (HDPE), and polyethyleneterephthalate (PET). The aim was to assess the degradation of these plastic articles caused by prolonged exposure to a harsh desert environment such as sunlight radiation. The reduction in molecular weight of the degraded plastics relative to that of the virgin plastics was estimated from the zero-shear viscosity-molecular weight relationship $\eta_0 = k\,(M_w)^a$. *The degradation was more pronounced with PS (THO6C) and PET2 (THO1BS) where the reduction in their molecular weight was estimated to be ~23%. There was a lack of sharp transition from glassy to rubbery state at the* T_g *of the degraded PS (THO6C) in comparison with the behavior of virgin PS. In addition, the degree of crystallinity of degraded PET1 (THO1BW) and degraded HDPE (THO2BW) was less than that of the virgin PET1 and virgin HDPE.*

Keywords: degradation, HDPE, molecular weight, PET, post-consumer, PS, Saudi Arabia

INTRODUCTION

Due to the sparsity of national parks, especially in the central province of Saudi Arabia, people find themselves forced to go to remote desert areas mainly during springtime for recreation purposes, i.e., picnicking and camping. Because of the lack of cleaning services in such areas,

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plastic materials that mainly are used for food packaging and plastic waste in the form of plates, cups, bottles and bags are left scattered around.

During the harsh weather in summer where temperature, wind, and humidity are very aggravating, discarded plastic materials are likely to be vulnerable to degradation, which, in turn, deteriorates the chemical and physical properties of such materials. Of these properties, reduction in molecular weight due to some forms of degradation such as chain scission is considered the most significant, since the majority of properties of polymeric materials depends greatly on molecular weight. Most importantly, in the context of current research, discarded plastic food packaging is subjected to severe ultraviolet (UV) radiation in the form of high intensity sunlight. The anticipated degradation of these plastic materials due to sunlight exposure would lead to materials with poor properties, especially the mechanical properties, and as these materials accumulate in the desert areas, their recyclability may not be beneficial for technical and economic reasons.

The main plastics used for food and drink packaging are high-density polyethylene (HDPE), polyethyleneterephthalate (PET), and polystyrene (PS). Photodegradation of these important plastics i.e., HDPE, PET, and PS, has been investigated in the past through a number of publications [1–13]. Degradation occurs mainly as a result of chain scission [1,10]. However, in HDPE, it was reported that crosslinking occurs in the early stages of photo-oxidation, and when time of exposure to UV light increases, chain scission prevails [1]. Depletion of UV stabilizers in HDPE due to photo-oxidation may lead to a decrease in thermo-oxidation-temperature (TOT) [1]. During the course of photodegradation, some polar groups may appear on the surface of degraded plastics. Examples of these chemical groups are carbonyl and hydroperoxide in HDPE [2,4], and carboxyl in PET [9,10].

Fillers have different effects on the degradation of plastics. Fillers with high UV reflection such as calcium carbonate ($CaCO_3$) act as good stabilizers for HDPE and hence minimize the intensity of photodegradation [2]. $CaCO_3$ acts as a barrier against UV light, inhibiting the formation of the γ-lactone group and hence increasing the UV stability of HDPE [6]. On the other hand, fillers with low UV reflection, such as mica, tend to speed up the degradation of HDPE when exposed to UV radiation [2]. PS films containing only 1 wt% of titanium dioxide (TiO_2) were found to be susceptible to degradation by sunlight [7]. UV-irradiated PET containing TiO_2 and barium sulfate ($BaSO_4$) was found to reduce in molecular weight by approximately 27% [9].

The addition of UV stabilizers, such as hindered amine, to some degraded HDPE articles may be a useful solution to recycle them for use in the original applications [3]. The addition of UV stabilizers to PET minimizes the formation of carboxyl end groups which is responsible for both surface and bulk degradation [10]. Research conducted on photodegradation of HDPE revealed that UV greatly promotes the environmental stress cracking in HDPE [5].

Rheological characterization, although not appreciated by most researchers, is a fast and useful tool to assess the degradation of polymeric materials. The reduction in molecular weight of a molten polymer, which implies its degradation due to chain scission, may be estimated by using zero-shear viscosity and molecular weight relationship which was reported in 1951 by Fox and Flory [14]

$$\eta_0 = \mathrm{k}(\mathrm{M_w})^{\mathrm{a}} \tag{1}$$

where η_0 is viscosity at very low shear rate, $\mathrm{M_w}$ is weight average molecular weight, and k and a are constants. For most polymers beyond their critical molecular weight ($\mathrm{M_c}$), a value of the constant a may be taken as 3.4, however, a higher value ~4.2 was reported for ultra-high molecular weight polymers [15].

In the current research, the aim was to assess the reduction in molecular weight of some food packaging plastic materials collected from remote desert areas, namely Thomamah, around Riyadh city, utilizing zero-shear viscosity data of such materials. These materials consist of several thermoformed and blow-molded articles made of PS, HDPE, and PET. This molecular weight assessment will be helpful to urge setting up plans for recycling of these valuable materials, which may be hindered due to degradation caused by prolonged exposure to aggressive sunlight.

EXPERIMENTAL

Materials

Degraded plastic materials in the form of PS cups and plates and HDPE and PET bottles were collected from the Thomamah area near Riyadh. PET materials were designated as PET1 and PET2. This PET2, mainly used for manufacturing soft drink bottles, has a slightly higher intrinsic viscosity value than that of the PET1, which is used for water bottles. These articles were washed to remove dust and dirt and then ground to a powder in a plastic grinder type IKA MF 10 using a sieve of size 0.5 mm. Virgin PS, HDPE, and PET were also used in this study to compare their properties with those of the

TABLE 1 Materials Used in this Study

Material	Code	Melt flow index (g/10 min)	Intrinsic viscosity (dl/g)
Virgin			
PS	PS100	13*	–
HDPE	HDPE	–	–
PET1	BC111	–	0.74*
PET2	BC112	–	0.82*
Degraded			
PS	THO6C	–	–
HDPE	THO2BW	–	–
PET1	THO1BW	–	–
PET2	THO1BS	–	–

*Provided by the manufacturer. All virgin plastics were supplied by Saudi Basic Industries Corporation (SABIC) in Riyadh, Saudi Arabia.

degraded materials. The details of the materials used in this study are given in Table 1.

Thermal Characterization

A DSC (type TA-Q10) was used to estimate melt and glass transition temperatures (T_m and T_g), and the heat of fusion of the virgin and degraded plastics (ΔH_f). Samples ranging from 10 to 15 mg of the materials tested were heated twice up to 200°C for PS and HDPE and 300°C for PET at a heating rate of 10°C/min.

Rheological Measurements

Viscosity vs. shear rate of the degraded and virgin plastics was obtained by a capillary rheometer type Rheo Cap 2000 (Thermo-Hakke). A 20:1 die was used, and an adaptor for nitrogen purge was connected to the inlet of cylinder for inert gas flushing in order to prevent degradation of the polymers at high temperature. Due to the different thermal behavior of the materials tested in this study, different temperatures were used to process these materials, i.e., 200, 190, and 256°C for degraded and virgin PS, HDPE, and PET, respectively.

RESULTS AND DISCUSSIONS

The curves representing melt viscosity vs. shear rate for all materials tested in this study are shown in Figures 1 to 4. A SYSTAT 10.2 software was used to fit the experimental data of viscosity—shear rate

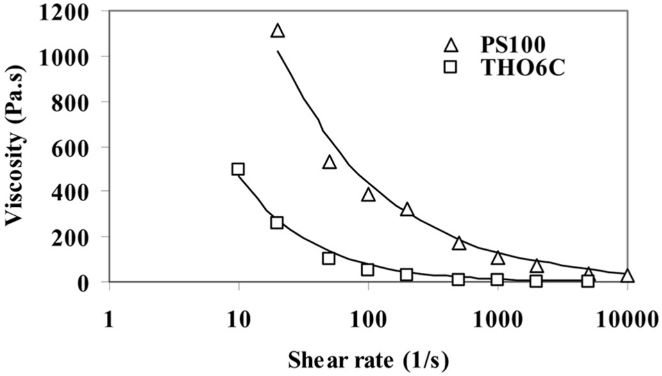

FIGURE 1 Viscosity vs. shear rate for the virgin and degraded PS; solid lines represent fitting of experimental data to the Cross model (Eq. 2).

relationship using nonlinear regression method. The experimental data were fitted to a three-parameter (Cross) model as follows:

$$\eta = \eta_0/(1 + (c\eta_0\dot{\gamma})^{1-n}) \tag{2}$$

where c is constant with the dimension of (area/force), and n is the flow index, while η_0 is the zero shear viscosity and $\dot{\gamma}$ is the shear rate.

Some symptoms of degradation were observed for the as-received degraded plastics, such as yellowish and grayish appearance and brittleness, especially with PS cups and plates. This indeed was supported by the contrast in melt flow behavior of these degraded

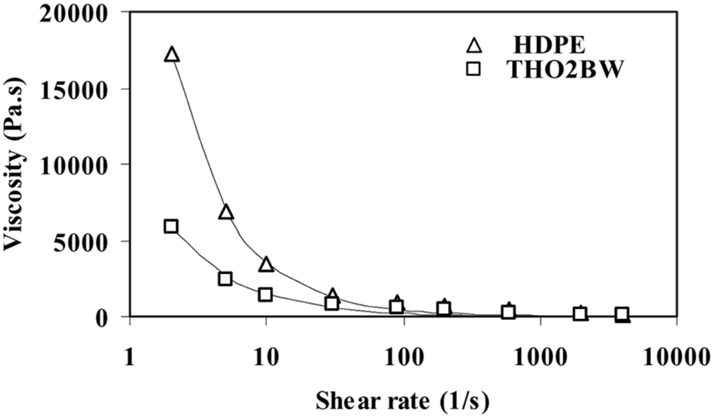

FIGURE 2 Viscosity vs. shear rate for the virgin and degraded HDPE; solid lines represent fitting of experimental data to the Cross model (Eq. 2).

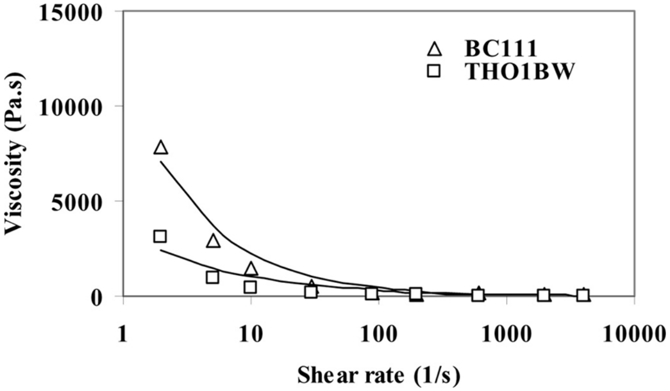

FIGURE 3 Viscosity vs. shear rate for the virgin and degraded PET1; solid lines represent fitting of experimental data to the Cross model (Eq. 2).

plastics in comparison with that of the virgin plastics. Figures 1 and 4 show that virgin PS (PS100) and virgin PET2 (BC112) have distinctly higher melt viscosity values at low and high shear rates than those of the degraded PS (THO6C) and degraded PET2 (THO1BS). On the other hand, as illustrated by Figures 2 and 3, virgin HDPE and virgin PET1 (BC111) show higher melt viscosity values than those of the degraded HDPE (THO2BW) and degraded PET1 (THO1BW), and this was observed only at lower shear rates. However, when the shear rate increases beyond 10 (1/s), the differences in melt viscosity values between virgin and degraded plastics diminish. This is not an unusual finding since polymers are shear-thinning materials where the

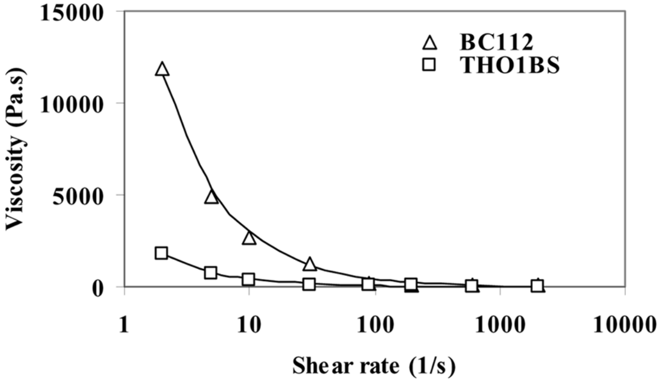

FIGURE 4 Viscosity vs. shear rate for the virgin and degraded PET2; solid lines represent fitting of experimental data to the Cross model (Eq. 2).

viscosity reduces to great extent upon shearing. The important finding here is the contrast in low shear viscosity values of the virgin plastics when compared to those of the degraded ones, since the reduction in melt viscosity at very low shear rate implies a reduction in molecular weight of the polymeric materials which in turn indicates the degradation of the material. For all degraded plastics tested in this study, a noticeable reduction in melt viscosity at low shear rates has been observed in comparison with those of the virgin ones (Figures 1 to 4). Thermal characterization, which is given by Table 2 and Figure 5, shows some differences in behavior and values of melting and transition of virgin and degraded plastics. One can clearly see from Figure 5 that degraded PS (THO6C) has no sharp transition at its T_g in contrast with the behavior of virgin PS, Figure 5a. Semicrystalline plastics, i.e., degraded PET1 (THO1BW) and degraded HDPE (THO2BW), on the other hand, have lower values of heat required to fuse the crystal structure than those of the virgin ones (see Table 2 and Figures 5b and 5c). This implies that the degree of crystallinity of these degraded plastics, i.e., THO1BW and THO2BW, has been reduced. This valuable information gained from thermal analysis comes as a support for the previous discussion of low shear viscosity reduction for degraded plastics, which was interpreted as degradation caused by prolonged exposure to sunlight.

For degraded and virgin polymers of the same type, Eq. (1) may be used to write relative zero shear viscosity as follows:

$$(\eta_0)_{\mathbf{d}}/(\eta_0)_{\mathbf{v}} = \{(\mathrm{Mw})_{\mathbf{d}}/(\mathrm{Mw})_{\mathbf{v}}\}^{\mathrm{a}}$$

or:

$$\mathrm{Log}\{(\mathrm{Mw})_{\mathbf{d}}/(\mathrm{Mw})_{\mathbf{v}}\} = (1/\mathrm{a}) \times \mathrm{Log}\{(\eta_0)_{\mathbf{d}}/(\eta_0)_{\mathbf{v}}\}$$

leading to:

$$(\mathrm{Mw})_{\mathbf{d}}/(\mathrm{Mw})_{\mathbf{v}} = 10^{(1/\mathrm{a})\times \mathrm{Log}\{(\eta_0)_{\mathbf{d}}/(\eta_0)_{\mathbf{v}}\}} \qquad (3)$$

TABLE 2 Thermal Characterization of Virgin and Degraded Plastics

Material	T_g (°C)	T_m (°C)	ΔH_f (J/g)
PS100	96	–	–
THO6C	98	–	–
BC111	79	254	33.56
THO1BW	77	251	23.68
HDPE	–	132	175.50
THO2BW	–	134	158.20

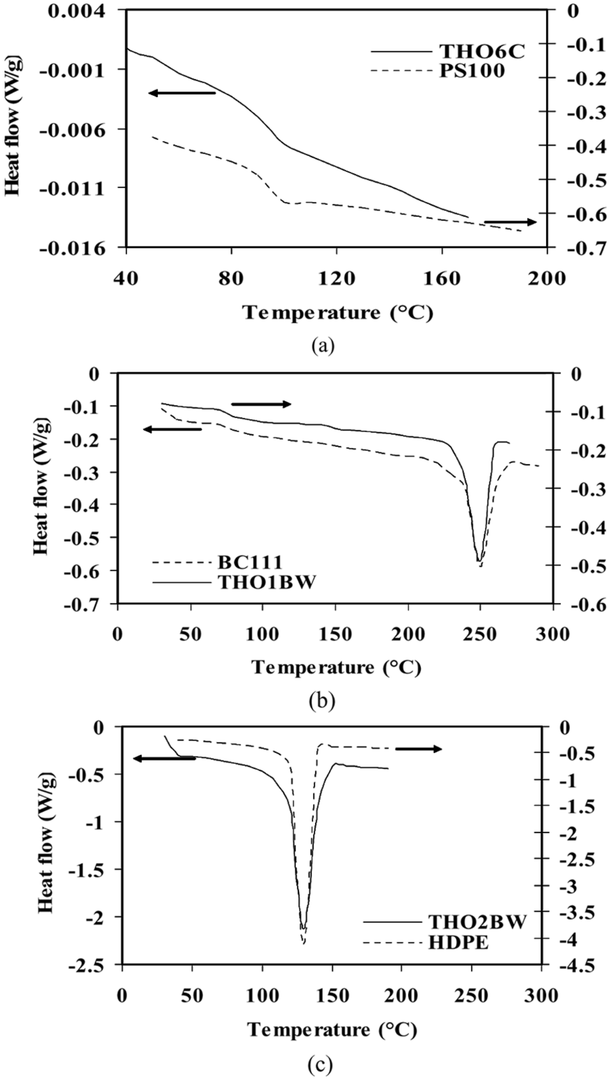

FIGURE 5 Thermal characteristics of degraded plastics in comparison to that of the virgin: (a) PS; (b) PET; and (c) HDPE.

where $(Mw)_\mathbf{d}$ is the molecular weight of degraded plastic while $(Mw)_\mathbf{v}$ is the molecular weight of virgin plastic. Zero shear viscosity, η_0, was obtained from fitting the experimental data to the three-parameter model in Eq. (2). Values of η_0 and correlation coefficient for the fitting, i.e. R^2, for all materials tested in this study are shown in Table 3. The

TABLE 3 Rheological Properties of Virgin and Degraded Plastics

Material	Zero shear viscosity (η_0) (Pa · s)	R^2 (from 3-parameter model fit)	Relative (η_0)	Log relative (η_0)	$(Mw)_d/(Mw)_v$
PS					
PS100	5.41×10^4	0.980	0.397	−0.401	$10^{(-0.401/a)}$
THO6C	2.15×10^4	0.992			
PET					
BC111	2.81×10^5	0.966	0.673	−0.172	$10^{(-0.172/a)}$
THO1BW	1.89×10^5	0.872			
BC112	11.19×10^6	0.996	0.403	−0.395	$10^{(-0.395/a)}$
THO1BS	4.51×10^6	0.996			
HDPE					
HDPE	3.22×10^6	0.998	0.680	−0.167	$10^{(-0.167/a)}$
THO2BW	2.19×10^6	0.990			

reduction in molecular weight of degraded plastics with respect to those of the virgin ones, i.e., $(Mw)_d/(Mw)_v$ given by Eq. (3), is shown in Table 3 as a function of the constant a. In order to estimate the percent of molecular weight reduction of the degraded plastics, the value for the exponent **a** was chosen as 3.5, which represents a mean of 3.4 and 3.6 that have been routinely used as exponent in the zero-shear viscosity molecular weight relation for linear polymers [16–20]. Figure 6 shows the reduction in molecular weight of the degraded plastics tested in this study—PS, PET, and HDPE. As can be seen clearly from Figure 6, the reduction in molecular weight was more pronounced in the case of degraded PS and PET2 ~23%. It is also shown in Figure 6 that in contrast to degraded PS and PET2, the estimated reduction in molecular weight for degraded PET1 and HDPE

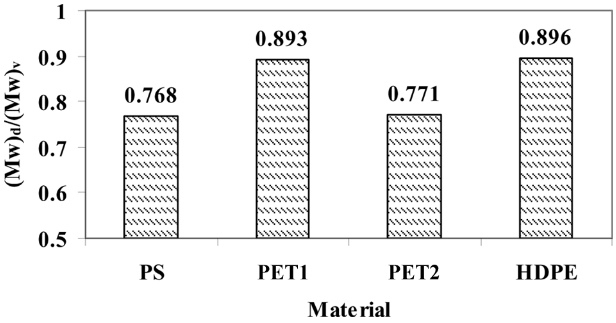

FIGURE 6 Reduction in molecular weight of degraded plastics relative to that of the virgin.

was lower ~10%. This may indicate that degraded PET1 and HDPE were exposed to sunlight in the remote Thomamah area for less time compared to degraded PS and PET2.

CONCLUSIONS

The current study gave an assessment on the degradation of some plastic food packaging articles reclaimed from the Thomamah area near Riyadh city. The degradation was manifested in a reduction of molecular weight of these degraded plastics. From the relative molecular weight estimation, using zero-shear viscosity-molecular weight relation, all degraded plastics tested in this study, i.e., PS, PET, and HDPE, have shown some degree of reduction in molecular weight in comparison to those of the virgin plastics. The largest reduction in molecular weight among the degraded plastics was observed with degraded PS (THO6C) and degraded PET2 (THO1SB) at ~23%.

REFERENCES

[1] Sharbel Luzuriaga, S., Kovarova, J., and Fortelny, I., *Polym. Deg. and Stab.* **91**, 1226 (2006).
[2] Yang, R., Yu, J., Liu, Y., and Wang, K., *Polym. Deg. and Stab.* **88**, 333 (2005).
[3] Vink, P., Rotteveel, R. T., and Wisse, J. D. M., *Polym. Deg. and Stab.* **9**, 133 (1984).
[4] Gulminea, J. V., Janissekb, P. R., Heisec, H. M., and Akcelrud, L., *Polym. Deg. and Stab.* **79**, 385 (2003).
[5] Li, R., *Polym. Deg. and Stab.* **70**, 135 (2000).
[6] Valadez-Gonzalez, A., Cervantes-Uc, J. M., and Veleva, L., *Polym. Deg. and Stab.* **63**, 253 (1999).
[7] Fa, W., Zan, L., Gong, C., Zhong, J., and Deng, K., *Applied Catalysis B: Environmental* **79**, 216 (2008).
[8] Edge, M., Hayes, M., Mohammadian, M., Allen, N. S., Jewitt, T. S., Brems, K., and Jones, K., *Polym. Deg. and Stab.* **32**, 131 (1991).
[9] Fechine, G. J. M., Rabellob, M. S., and Souto-Maior, R. M., *Polym. Deg. and Stab.* **75**, 153 (2002).
[10] Fechine, G. J. M., Rabellob, M. S., Souto-Maior, R. M., and Catalani, L. H., *Polymer* **45**, 2303 (2004).
[11] Day, M. and Wiles, D. M., *J. Appl. Polym. Sci.* **16**, 175 (1972).
[12] Day, M. and Wiles, D. M., *J. Appl. Polym. Sci.* **16**, 191 (1972).
[13] Day, M. and Wiles, D. M., *J. Appl. Polym. Sci.* **16**, 203 (1972).
[14] Fox, T. G. and Flory, P. J., *J. Phys. Colloid Chem.* **55**, 221 (1951).
[15] Tate, S. and Narusawa, H., *Polymer* **37**, 1583 (1996).
[16] Gregory, D. R. and Watson, M. T., *J. Polym. Sci.* **30**, 399 (1970).
[17] Montfort, J. P. *Polymer* **17**, 1054 (1976).
[18] Linliu, K. and Chu, B., *Polymer* **36**, 2265 (1995).
[19] White, J. L. and Kondo, A. J., *Non-Newtonian Fluid Mech.* **3**, 41 (1977/1978).
[20] Raju, V. R. Smith, G. G., Marin, G., Knox, J. R., and Graessley, W. W. J., *Polym. Sci., Phys. Ed.* **17**, 1183 (1979).