



# EFFECT OF RECYCLING OF THERMOPLASTICS: EVALUATION OF THE PROPERTIES OF MIXTURE OF VIRGIN AND RECYCLED HIGH-DENSITY POLYETHYLENE

Neaz Ahmed<sup>1</sup> and Javaid H. Khan<sup>1</sup>

*1: Center for Refining & Petrochemicals, Research Institute, KFUPM, Dhahran-31261, Saudi Arabia*

*E-mail: jhkhan@kfupm.edu.sa*

## ABSTRACT

*Plastic recycling was carried out on the virgin HDPE, mixture of both collected recycled HDPE material and virgin HDPE. Processing aids in terms of certain percentage of anti-oxidants and slipping agents were added to virgin and 50/50 mixture of HDPE recycled material. The specific emphasis was placed on the effect of thermal stabilizer concentration in the base material during processing cycle. Thermo-oxidative degradation was observed in polymeric material during injection molding cycle. The performances of resulting reprocessed plastics were monitored using Fourier transformation infra-red (FTIR), Differential scanning calorimeter (DSC), and Mechanical properties. The results clearly reveal the rapid thermo-oxidative degradation of the 50/50 mixture of fresh and recycled HDPE material after three re-processing cycles, which can be attributed to the antagonistic mixing effect of two materials and the early loss of added anti-oxidant and processing stabilizers. The better processing stability can be achieved by incorporating appropriate percentages of processing stabilizers in polymer resin up-to limited number of processing cycles.*

**Keywords:** *High-density polyethylene, Recycling, Thermal-degradation*

المخلص

(FTIR)

(DSC)

## 1. INTRODUCTION

Plastics have become an indispensable part of modern life. Cars, computers, baby-bottles, telephone, clothing, packaging; no aspect of our society is untouched by plastics. Their versatility of physical properties and the unique formability have made them ubiquitous. These intrinsic physical properties made polymer eminently suited to recycling. Plastics have indeed been recycled in various ways ever since their introduction over decades ago. With increasing application and decreasing prices, plastics became the symbol of disposability in consumerism and hence an inevitable object of concern in the relatively recent heightened public awareness of environmental issues.

Recycling is only sensible if the cost of processing the scrap at the end of its life is less than the value of the recycle produced. Having been promoted to a positive life cycle may be repeated in principle any number of times [Voute, 1994]

Thermoplastics were found by others to restore mechanical properties in recycled polyethylene contaminated by other polymers by improving compatibility between them and the principal polymer [Hope et al., 1994].

World production of plastics has increased from an estimated one million tons in 1940 to over 120 million tons in 1993. Every nation is concerned with the disposal of industrial effluents and post-consumer waste and seeking the means to develop effective reclamation and recycling policies. The waste products arising from plastics packaging, which accounts for about 35 percent of the total plastics consumption, has contributed to the perception of plastics as a major environmental problem and to the introduction of legislation prescribing targets for recycling. Many nations are now enhancing their confidence upon recycling, especially that of packaging as an alternative to disposal. United States produce about 165 million tons of solid waste per year but the number of landfills for municipal solid waste has fallen there by 32 percent. The waste management problem is more pressing for the industrialized countries and the developing nations to take precautions and learn from the bitter experiences of the developed world [Goldstein, 1989].

The purpose of waste management approach beyond the disposal is to ensure the difficult task that our environment sustains the least possible damage from the masses we discard every day. Dumps are overflowing and waste stream is becoming more heterogeneous and less readily degradable. The need to find substantial alternatives to landfills is clear. Plastics represent about nine percent by weight and twenty percent volume of the total solid waste [Anonymous, 1992].

Some environmentalists have strong view that plastics should be banned altogether because of the waste disposal problem. But this is not a logical solution to the problem. Because plastics are cheap, convenient and durable materials and hence have penetrated in every sphere of human lives. Nevertheless, the plastics industries have shown a slow response to waste problems. However, they would have to adopt appropriate waste management programs. For plastics waste, as the other forms of waste, the solution would be developed to make the most

use of the source reduction by recycling, incineration and landfills in that order. Disposal of the thermoplastics can be made through several methods such as incineration, landfills and recycling. Although, of the proposed approaches, recycling presents the most feasible option. Through recycling these materials can be turned into many different and valuable products, thus recovering much more efficiently the value of the original material. Secondly, incineration of several polymers such as PVC, PAN, and polyurethanes may pollute the environment with toxic fumes [Carlsson and Wiles, 1976].

An experimental basis for the prediction of the properties of neat HDPE and mixture of virgin and recycled HDPE during reprocessing of polymer is presented. Experiments were performed that describes the loss of polymer properties as a function of processing cycles and the concentration of thermal stabilizers used. Polymer properties that are important in characterization and quality control, such as melt flow index, percent elongation, tensile strength, carbonyl index and percent crystallinity were evaluated for the samples under study.

## **2. EXPERIMENTAL**

### **2.1 Sample Preparation**

Six types of high-density polyethylene (HDPE) samples were prepared through injection molding. HDPE grade M-80064 was used as virgin HDPE material and the recycled shredded material (HDPE crates) was collected from the local polymer recycling company.

Processing additives in the form of antioxidants and slipping agents were added to the virgin and recycled HDPE materials. Most commonly used hindered phenols and phosphite types of processing stabilizers viz, Irganox 101 and Irgafos 168 (CIBA Co. Switzerland) with 1 percent of a slipping agent e.g. calcium stearate were added during the injection molding of the materials. The final zone temperature of injection molding machine during extrusion of the polymeric material was set at 230°C.

The following six types of virgin HDPE and 50/50 recycled and virgin HDPE combination samples were extruded up to five molding cycle in the injection molding machine with the addition of three different percentage of processing stabilizers (Irganox and Irgafos) and 0.1% of Ca stearate.

**Type 1:** 1<sup>st</sup>-extrusion: Virgin HDPE with 0.05%, 0.1%, 0.2% Irganox and Irgafos

**Type 2:** 3<sup>rd</sup>-extrusion: Virgin HDPE with 0.05%, 0.1%, 0.2% Irganox and Irgafos

**Type 3:** 5<sup>th</sup>-extrusion: Virgin HDPE with 0.05%, 0.1%, 0.2% Irganox and Irgafos

**Type 4:** 1<sup>st</sup>-extrusion: 50/50 Virgin/recycled HDPE with 0.05%, 0.1%, 0.2% Irganox and Irgafos

**Type 5:** 3<sup>rd</sup>-extrusion: 50/50 Virgin/recycled HDPE with 0.05%, 0.1%, 0.2% Irganox and Irgafos

**Type 6:** 5<sup>th</sup>-extrusion: 50/50 Virgin/recycled HDPE with 0.05%, 0.1%, 0.2% Irganox and Irgafos

## **2.2. Characterization Methods:**

The characterization of the samples was done by Fourier transformation infrared (FTIR) spectroscopy, Differential scanning calorimeter (DSC), Mechanical strength measurement and Melt flow index.

FTIR was utilized to observe the change in the carbonyl absorbance in the region of 1710-1730  $\text{cm}^{-1}$ . The FTIR spectra were recorded using Perkin-Elmer FTIR model 1650 spectrophotometer. The instrument was calibrated using the standard polystyrene film.

A Perkin-Elmer, model DSC-4 differential scanning calorimeter, determined the thermal properties. The calibration was carried out using Indium, having melting point 156.6°C, transition energy 6.8 Cal/gram and atomic weight of 114.82.

Elongation and tensile properties were determined by an Instron mechanical testing system, model 4301. A long travel extensometer was used for determining the mechanical properties. The cross head speed of 100 mm/min was maintained under the limitation of ASTM standard D-882.

Melt flow index (MFI) determination was carried out using a Zwick's Flow Test Apparatus, model D-7900T 4105-01/02. The experiments were carried out at 190°C and 2.16 kg load following the ASTM standard D-1238.

## **3. RESULTS AND DISCUSSION**

Studies on polymer blends or mixtures of polymers are not only important from scientific viewpoint but are subject of considerable commercial interest. Blends of different polymers can result in the material with wide variety of tailor-made properties. Crystalline-crystalline polymers have been studied and it was found that in most of the cases 50:50 composition of the polymer gave the best compromise of good mechanical properties, heat stability and outdoor weathering [Kolawole and Agboola, 1982], [Escala and Stein, 1979].

The useful lifetime of a polymer can be extended sufficiently to meet design requirements for long-term application through proper thermal stabilization. The stabilization of polymers is still undergoing transition from an art to a science, as the mechanism of degradation becomes more fully understood. A scientific approach to stabilization at all stages of polymer can be developed through understanding process and degradation reactions of the polymers [Hawkins, 1984].

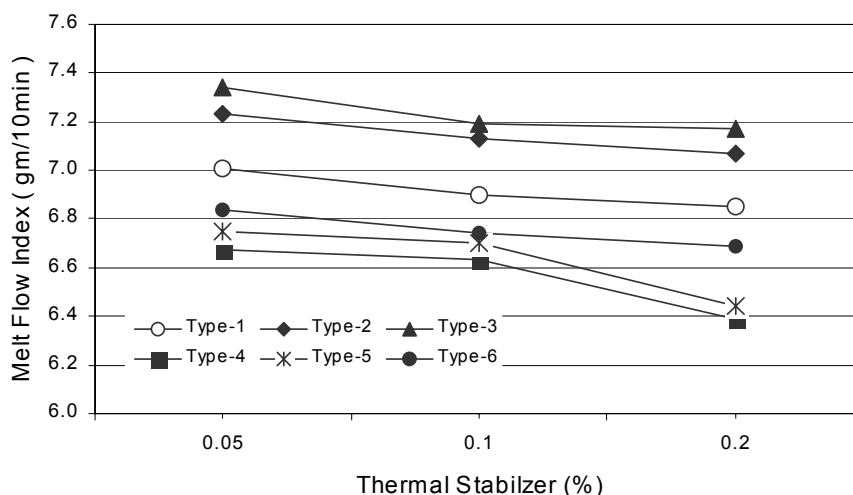
Recycled material can be transformed into useful products requiring from one to three or more processing steps, even today's new and highly sophisticated technology. Each of these processing steps is usually carried out at high temperatures, which is usually attained by the combination of high pressure and shear in processing machine. The molecular structure is drastically altered and produce non-uniform product with undesirable properties if proper stabilization of base polymer material is not done [Ghani, 1987].

The present work describes the effect of thermal stabilizers concentration on number of molding cycles at 230°C on the chemical, thermal, mechanical and melt flow index properties of the recycled and fresh HDPE materials. Three combinations 0.05, 0.1 and 0.2 percent of thermal stabilizers were used for recycling the materials under study up to five extrusion cycles. In each extrusion cycle 0.1 percent of calcium stearate was used as slipping agent.

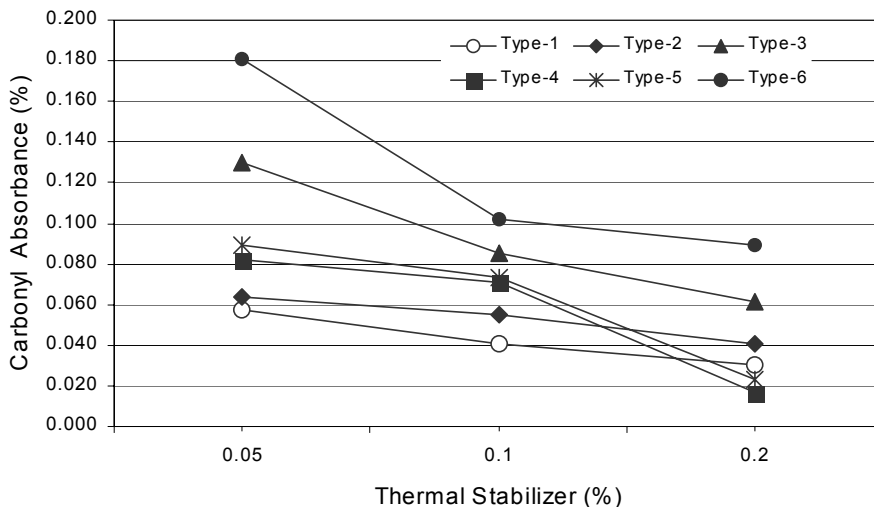
Flow of the plastic in the mold is quite important to *ensure adequate fill*; to avoid short shots as well as voids. The Melt Flow Index (MFI) is one of the indices used to characterize the behavior of molten plastic.

Figure 1 represents melt flow index of virgin HDPE and the mixture of virgin and recycled HDPE. The effects of compatibility can be seen in the 50/50 mixture as lower values of MFI as compared to the virgin HDPE alone. This being an indication that the backbone of polymer material is intact and no chain breaking has started in the early cycles of extrusion. Degradation of polymeric materials generally resulted in reduced molecular weight, which directly exhibit poor physical properties. The higher values of MFI can be clearly seen in Figure 1 as the concentration of thermal stabilizers are reduced from 0.2 to 0.05 percent. The increased value of MFI is a clear indication of thermo-oxidative degradation of polymeric material during each extrusion cycle.

The 4.7 percent increase in MFI was observed during 1<sup>st</sup> to 5<sup>th</sup> molding cycle, when 0.05 percent thermal stabilizers was used, while an increase of 4.6 percent was observed during same number of molding cycle with 0.2 percent of thermal stabilizers in virgin HDPE. The 50/50 mixture showed 2.5 percent increase in MFI while using 0.05 percent of thermal stabilizers during 1-5<sup>th</sup> molding while a drastic increase of 4.7 percent in MFI was observed in fifth molding cycle with 0.2 percent of stabilizers. This shows an antagonistic mixing effect of thermal stabilizers with the recycled mixed material due to higher degradation at 5<sup>th</sup> molding cycle.



**Figure 1.** Change in melt flow index as a function of processing stabilizers concentration.



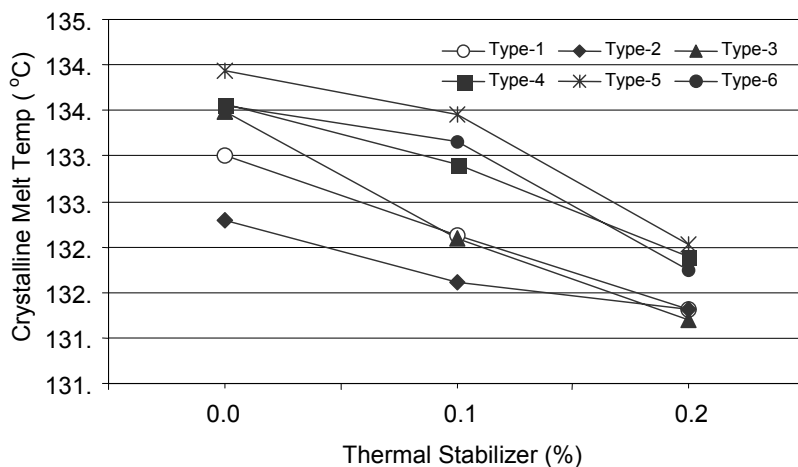
**Figure 2.** Change in carbonyl absorbance as a function of processing stabilizers concentration

Figure 2 represents the change in Carbonyl absorbance as a function of thermal stabilizers concentration used during each extrusion cycles. The overall increase in carbonyl index was observed for all the recycled samples as the concentration of thermal stabilizers dropped from 0.2 percent to 0.05 percent. The higher increase of 128 percent in carbonyl index was observed for the virgin HDPE material with 0.05 percent thermal stabilizers as compared to 44.6 percent for 0.2 percent thermal stabilizers during 1<sup>st</sup>–5<sup>th</sup> extrusion cycles. While the increase of 120 percent in the carbonyl index with 0.05 percent thermal stabilizers and 38.5 percent increase with 0.2 percent stabilizers was observed during extrusion cycles for 50/50 mixture material. It is evident from the enhanced trend in carbonyl absorbance that thermo-oxidative degradation of material is taking place as the concentration of processing stabilizers are reducing from 0.2 to 0.05 percent during each extrusion cycle.

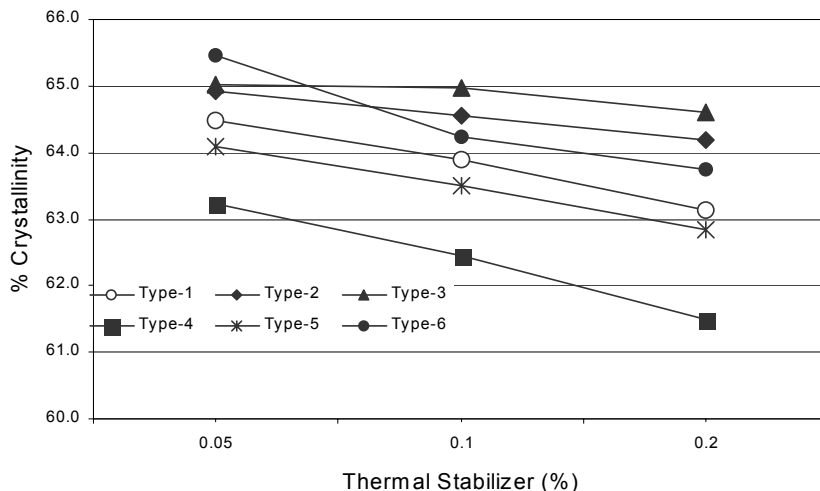
Figure 3 and figure 4 represents the change in crystalline melt temperature and percent crystallinity with the change in thermal stabilizers concentration. It is evident from the figure that the crystalline melt temperature is not affecting much with the change in processing stabilizers concentration. It is almost keeping the same values with the difference of 1–2°C for all samples having varied stabilizers concentration during each extrusion cycles for both type of materials.

The increasing trend of percent crystallinity can be seen in figure 4, as the concentration of thermal stabilizers decreases from 0.2 to 0.05 percent for all the extrusion cycles for both types of materials. The increase in percent crystallinity of the polymeric material is a direct indication of degradation of material during processing cycles. The increase of 0.8 percent crystallinity was observed for the 0.05 percent stabilized virgin HDPE during 1<sup>st</sup>–5<sup>th</sup>

extrusion cycles. While the increase of 2.3 percent from its initial value was observed with 0.2 percent stabilized samples during same extrusion cycles. The increase of 3.5 percent from its initial value in crystallinity was observed for the 0.05 percent stabilized 50/50 mixture material during 1<sup>st</sup>-5<sup>th</sup> molding cycles. While the increase of 3.6 percent from the initial value was observed for the samples stabilized with 0.2 percent of processing thermal stabilizers. It was noted that the samples stabilized with 0.2 percent of stabilizers have gained higher values of crystallinity during fifth extrusion cycle. This could be due reverse mixing effect of thermal stabilizers with the recycled material and could be the reason of fast degradation of the material.



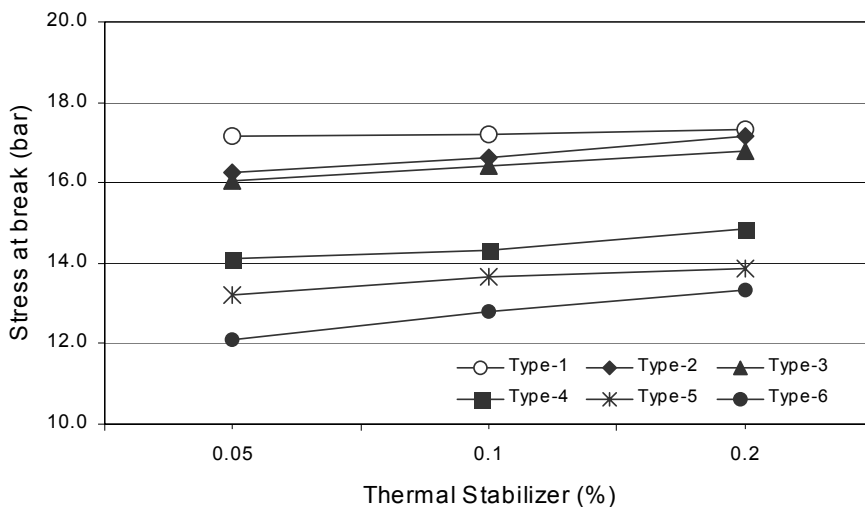
**Figure 3.** Change in crystalline melt temperature as a function of processing stabilizers concentration



**Figure 4.** Change in percent crystallinity as a function of processing stabilizers concentration

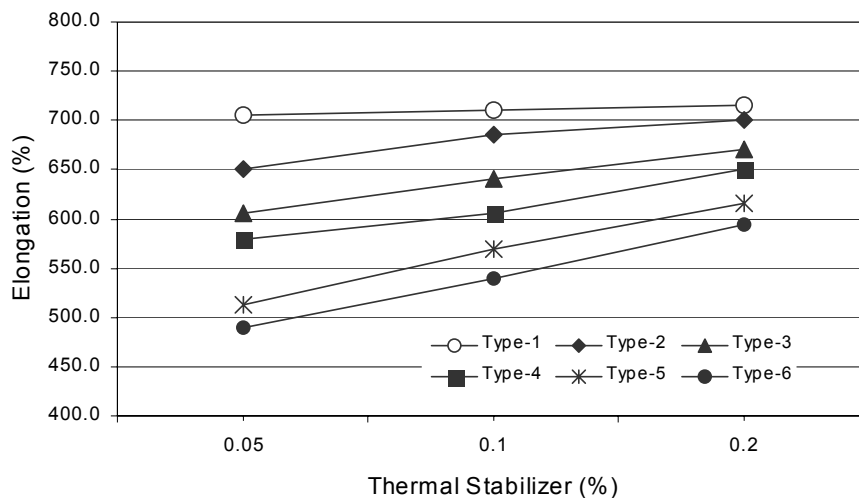
Figure 5 and figure 6 shows change in stress at break and percent elongation for extruded samples as a function of thermal stabilizers concentration in the base polymer materials. It can be seen from figure 5 that the decreasing trend in stress at break follows if the stabilizers concentration is dropped from 0.2 percent to 0.05 percent during extrusion cycles for both the materials. The 6.5 percent drop from its initial value was observed for the samples stabilized with 0.05 percent of stabilizers for virgin HDPE during 1<sup>st</sup>–5<sup>th</sup> extrusion cycles. The drop of 3 percent was noted for the samples stabilized with 0.2 percent of stabilizers during same number of extrusion. The drop in stress at beak for 50/50 mixture material stabilized with 0.05 percent stabilizers was observed 14.3 percent during 1<sup>st</sup>–5<sup>th</sup> extrusion cycles. While the drop of 10.1 percent was observed for the samples stabilized with 0.2 percent of stabilizers for the same number of extrusion.

Figure 6 also present decreasing trend in percent elongation for both types of polymeric materials if the concentration of processing stabilizers decreases from 0.2 percent to 0.05 percent during 1<sup>st</sup>–5<sup>th</sup> extrusion cycles. The decrease of 14.1 percent was observed for the virgin HDPE material stabilized with 0.05 percent of thermal stabilizers during 1<sup>st</sup>–5<sup>th</sup> extrusion cycles. While the drop of 6.2 percent in elongation was noted for the samples stabilized with 0.2 percent of thermal stabilizers during same number of extrusions. The other 50/50 mixture material showed the drop of 15.5 percent in elongation from its initial value for the samples stabilized with 0.05 percent of thermal stabilizers. While the drop of 3.4 percent was observed for the samples stabilized with 0.2 percent of thermal stabilizers during 1<sup>st</sup>–5<sup>th</sup> extrusion cycles.



**Figure 5.** Change in stress at break as a function of processing stabilizers concentration





**Figure 6.** Change in percent elongation as a function of processing stabilizers concentration

These drops in stress at break and percent elongation clearly reveals that the chain breaking is taking place in the backbone of polymer matrix. The mechanical properties results in term of stress at break and percent elongation showed good synchronism with the increase in percent crystallinity, carbonyl absorbance and melt flow index as reported above. The reported results are complimenting each other and depicting that optimal 0.2 percent of thermal stabilizers are playing a key role in maintaining the polymer properties even up to fifth extrusion of the material.

#### 4. CONCLUSION

1. The higher value of MFI of the polymer materials after fifth molding cycle indicates that the chain breaking in the polymer backbone (a decrease in molecular weight) is occurring. This provides an information that the polymer material is degrading as the number of extrusion is increasing.
2. The optimal 0.2 percent of the thermal stabilizers used for the fifth extrusion shows good stability of the virgin HDPE material but not for the 50/50 mixture.
3. The concentration of added thermal stabilizers are playing an important roll for the stability of the polymeric material to be used up to three cycle of extrusion in both cases.
4. The increase in melt flow index, percent crystallinity and carbonyl absorbance and decrease in percent elongation and stress at break were observed for all the sample during each extrusion cycle as the concentration of thermal stabilizers reduced from

0.2 to 0.05 percent. The crystalline melt temperature has not shown much change in its values.

5. The phosphite and hindered phenol types of thermal processing stabilizers retained the polymer properties up to third extrusion, which permit the material to be used for optimal applications in quality products.
6. The 0.05 and 0.1 percent of used thermal stabilizers have shown higher thermo-oxidative degradation as compared to 0.2 percent at every extrusion cycle. But to economize the stabilizers cost the 0.05 and 0.1 percent concentrations can also be used for recycling of material up to three extrusions with better polymer properties.
7. The virgin HDPE material with the same percentage of thermal stabilizers showed higher rate of thermal degradation at each extrusion cycle as compared to mixture of recycled and virgin HDPE.
8. The 50/50 mixture showed the highest rate of degradation at fifth extrusion cycle due to the antagonistic effect of added stabilizers and recycled polyolefin material.

## ACKNOWLEDGEMENT

The authors thank the Research Institute, King Fahd University of Petroleum and Minerals for the support of this scientific technical research.

## REFERENCES

1. Anonymous, 1992, *Plastics waste management*: 4 Ciba-Geigy, Switzerland,
2. Carlsson, D. J. and Wiles, D. M., 1976, *J. Macromol. Sci. Rev. Macromol. Chem. Phys.*, C14, p 65.
3. Escala, A. and Stein, R. S., 1979, *Advances in Chemical Series*, vol. 176, p 455.
4. Ghani, R., 1987, "Processing, heat and light stabilization of polyolefins," *Seminar at KFUPM/ RI, Dhahran, Saudi Arabia*.
5. Goldstein, G., 1989 *Mechanical Engineering*, August, pp. 544,
6. Hawkins, W. L., 1984, *Polymer degradation and stabilization*, published by Springer-Verlag, Berlin.
7. Hope, P.S., Bonner, J.G. and Miles A.F., 1994, "Plastics, Rubber and composites processing and applications, 22, 147-158,
8. Kolawole, E. G. and Agboola, M.O. 1982, *Journal of applied Polymer Science*, vol. 27, p. 2317.
9. Voute, C., 1994, "Why recycle?," *Proc. Recycling council annual seminar*, Birmingham, U.K.