

## Mechanical Properties And Kinetics Of Weight Loss Of Polypropylene Waste Plastic Within The Very Low Extent Of Weight Loss Under Iso-Thermal Conditions.

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**ABSTRACT:** Polypropylene is one of the main raw materials used in plastic industry of Sri Lanka for manufacturing domestic plastic products. This paper was focused to study weigh loss of polypropylene isothermal degradation, it's mechanical properties, obtained order of reaction and as well as toughness variation at different temperature. However very low extent of weight loss (0.3% by mass) at iso-thermal conditions in the range of temperature 80 °C to 140 °C has significantly affected to the tensile strength, breaking strength, strain at break, and yield strength due to the evaporation of more volatile substances. It was observed variation of order of reaction at different temperature.

**Keywords** - Waste Polypropylene, Mechanical property, Kinetics of weight loss, Iso-thermal conditions.

### I. INTRODUCTION

Polypropylene is one of the most important commercial polymers used in manufacture of a range of plastic products. In Sri Lanka, it is used in manufacturing the plastic furniture and range of plastic products for domestic applications. Custom data of the last ten years indicates growth pattern of polypropylene based plastic manufacturing industry in Sri Lanka [1]. Recycling of plastics has become a small scale industry as a solution for the accumulation of plastics in the environment. The lowering of the physic-mechanical properties of polymer products is mainly due to the (a) decomposition of additives, (b) evaporation of volatile ingredients, (c) catalyst residues containing Ti, Al and Cl, (d) unsaturated groups formed during polymerization by chain transfer, or disproportionation of growing chain ends, and (e) carbonyl groups, introduced by carbon monoxide impurities in the monomer and through oxidation, (f) reactive forms of oxygen such as ozone (O<sub>3</sub>) which is present in the atmosphere and singlet oxygen (<sup>1</sup>O<sub>2</sub>) which can be produced inside the polymer by quenching of UV excited species by ground-state oxygen (<sup>3</sup>O<sub>2</sub>), (g) cross-linking and chain scissions of polymer molecules. The change in physico-mechanical properties of polymer products is typically very slow process under the tropical climate condition. Additives are used to optimize the physico-mechanical properties, minimize the degradation under the environmental conditions and during the processing due to heat and mechanical stress. The knowledge of the change in physico-mechanical properties of plastics with the kinetics of weight loss is important to estimate the level of physico-mechanical properties of plastic waste for the recycling process. The standard power law kinetics model has been used to study the thermal degradation of polymer. The equation (1) given below is the typical power law of Arrhenius equation used in studying the kinetics of polymers degradation under the isothermal condition. It is a combination of the effect of temperature and content of material remained to react [2].

$$\frac{d\alpha}{dt} = (1 - \alpha)^n A e^{-\frac{E}{RT}} \text{-----(1)}$$

Parameters of the equation (1) which  $\alpha$  is the relative mass loss of the polymer at a time  $t$ ,  $n$  is the order or power of the kinetic equation,  $T$  is the absolute temperature,  $R$  is the gas constant,  $A$  is the pre-exponential factor and  $E$  is the activation energy. In the equation (2) the parameter  $W_0$  is the initial mass,  $W_t$  is mass at time  $t$  and  $W_f$  is mass of sample at the end of experiment. The rate constant  $k$  is a product of  $A$  and exponential of  $-E/RT$  in

Arrhenius equation,  $k = A e^{-\frac{E}{RT}}$

$$\alpha = \frac{W_0 - W_t}{W_0 - W_f} \text{-----(2)}$$

Kissinger, Fridman and Ozawa are the other proposed models used for evaluating the activation energy and pre-exponential factor in Arrhenius equation for the kinetics of polymer degradation [3]. Number of alternative models proposed in literature are infinite Number of Parallel Reactions Model, the Weak Bond Model, Consecutive Reaction Models and, Simha and Wall Model. The complexity in practical applications of these models was reviewed by R. W. J. Westerhout and *et al* [4]. However, the simplicity of power model to use in practical purpose is the main advantage.

A first order kinetic equation has been used in most of literature to study the thermal degradation of polymer. The literature values of activation energy and frequency factor of degradation kinetics of polypropylene indicate the inconsistency [4-9]. Thermo-gravimetric analysis (TGA) under the isothermal and non-isothermal condition is a common technique to study the kinetics of polymer degradations. The degradation kinetic under isothermal conditions is preferred since the interpretation of data is simple and one parameter (conversion  $\alpha$ ) is monitored during an experiment, instead of two parameters,  $\alpha$  and T, in the case of non-isothermal methods. Huimin Wang *etal* [10] has shown the change in the activation energy during the entire degradation process of polymer. Change in activation energy of degradation suggests a sequence of reactions and demonstrate complex kinetics of polymer degradation. Chemical structures of polymer molecule are stable below the 100 °C temperature and usually stable 100 °C - 200 °C range. However, degradation is very prominent at 400 °C to 600 °C since the thermal energy at that temperature range is sufficient for energy requirement of bond breaking which have 150- 400 kg mol<sup>-1</sup> [11].

Degradation of plastics and activation energies of reactions during the degradation were studied at higher temperature above 200 °C. The attention of change in mechanical and spectroscopic properties prolong exposure to the temperature around the 100 °C is very rare. Loss of these organic additives such as stabilizers and plasticizers in the matrix will significantly affect to inferior quality of the physical and mechanical properties of commercial plastic before the real degradation of polymer molecules. The objective of this research project is to study polypropylene waste plastic as a model plastic material to evaluate the change in mechanical properties, spectroscopic properties, with the kinetics of weight loss nearly up to 0.3% (as w/w%) under four different isothermal conditions at 80 °C, 100 °C, 120 °C, 140 °C.

## II. MATERIAL AND METHOD

Polypropylene plastic boxes used in ice cream industry were selected in this study as a model material. Flat surface area of boxes with 0.2mm thickness was selected for dumbbell shaped test piece. Each set of samples were separately kept isothermal conditions at 80, 100, 120, 140 °C. At each time three pieces were examined for the measurements of weight loss, melt flow index (MFI), stress strain behavior and studied the relative changes in FTIR spectrums. In each set of three samples, average of measurements was used for the Kinetics of weight loss and MFI. Integrated version of Arrhenius equation was used to analyze the kinetics of weight loss within three different iso-conversional limits of  $\alpha$  from 0.0 to 0.4, 0.4 to 0.6 and 0.6 to 0.9, [12].

## III. RESULTS AND DISCUSSION

Table 1 shows the variation of activation energy, pre-exponential factor, power of the kinetic equation, rate constant and correlation coefficient ( $r^2$ ) in the range of  $\alpha$  from zero to 0.4, 0.4 to 0.6 and 0.6 to 0.9 respectively at the four different isothermal conditions. Activation energy of the kinetics of weight loss at these four different temperature within the three different ranges of  $\alpha$  was very low compared to the literature values (217 kJ mol<sup>-1</sup>) reported for the degradation process at the temperature above 200 °C. The calculated values of pre-exponential factor at the four different isothermal conditions were also very low compared to the range  $1.5 \times 10^{12}$  to  $1.7 \times 10^{12}$  s<sup>-1</sup> K<sup>-0.5</sup> reported in the literature. Low activation energy and very low pre-exponential factor indicate physical nature of the process during these four different isothermal conditions below 200 °C. Melt flow index is an indication of average molar mass of polymer. The melt flow index of commercial PP samples is 4.3 g/10 min. MFI of samples are not significantly changed even after 14 hours period of time under the different isothermal conditions. It suggested that the 14 hours duration under the isothermal conditions was not sufficient for the real degradation of polymer molecules.

The activation energy has not significantly changed and nearly 26 KJ mol<sup>-1</sup> within the four different temperature in the range of  $\alpha$  from zero to 0.6. However, it has increased to 62 KJ mol<sup>-1</sup> as  $\alpha$  exceeds 0.6. It indicates the effect of textural changes as a result of evaporation of volatile materials to increase the energy barrier for the evaporation of volatile substances or declining of easily volatile substance. Order of the kinetic equation has changed from 2 to  $\frac{1}{5}$  in the range of  $\alpha$  from zero to 0.9 and these values agreed with the values in literature [13].

Figure 1 shows the increasing pattern of power of kinetic equation in the range of  $\alpha$  from 0.0 to 0.4 with temperature. It is an indication of the linear relation between the textural changes with thermal expansion for the evaporation of easily volatile substances.

Table 1: Kinetic parameters at the four different temperature.

Range of conversion $\alpha = 0.0 - 0.4$				
Temperature	80 °C	100 °C	120 °C	140 °C
$E$ (KJ/ mol)	26.9	26.80	27.5	26.6
$A$ ( $\text{min}^{-1}$ )	32.52	32.52	32.52	32.52
$r^2$	0.9772	0.9633	0.9921	0.9698
$n$	2/5	6/5	7/5	2
$K$ ( $\text{min}^{-1}$ )	$3.5 \times 10^{-3}$	$5.8 \times 10^{-3}$	$7.2 \times 10^{-3}$	$1.4 \times 10^{-2}$
Range of conversion $\alpha = 0.4 - 0.6$				
Temperature	80 °C	100 °C	120 °C	140 °C
$E$ (KJ/ mol)	26.06	25.0	25.5	26.0
$A$ ( $\text{min}^{-1}$ )	12.90	12.90	12.90	12.90
$r^2$	0.9592	0.9632	0.9925	0.9839
$n$	1/5	8/5	1	3/5
$K$ ( $\text{min}^{-1}$ )	1.8 X	4.1 X $10^{-3}$	5.2 X	6.7 X $10^{-3}$
Range of conversion $\alpha = 0.6 - 0.9$				
Temperature	80 °C	100 °C	120 °C	140 °C
$E$ (KJ/ mol)	62.35	61.24	62.91	61.80
$A$ ( $\text{min}^{-1}$ )	$3 \times 10^{-4}$	$3 \times 10^{-4}$	$3 \times 10^{-4}$	$3 \times 10^{-4}$
$r^2$	0.9935	0.9197	0.9618	0.9877
$n$	1/5	2/5	3/5	2/5
$K$ ( $\text{min}^{-1}$ )	$2.0 \times 10^{-4}$	$8.5 \times 10^{-4}$	$1.4 \times 10^{-3}$	$4.9 \times 10^{-3}$

However, such linear relation was not prominent as  $\alpha$  exceeds 0.4. It indicated the complexity of the textural changes with decreasing the amount of more volatile substances and commencing the evaporation of less volatile substance as the magnitude of  $\alpha$  exceeds 0.4. The magnitude of rate constant within the three ranges of  $\alpha$  decrease with the temperature as expected and Figure 2 shows the agreement between  $\ln K$  and  $1/T$ . Table 1 indicates that the rate constant is also a function of  $\alpha$  at a constant temperature. Rate constant has decreased with the range of  $\alpha$  from 0.0 - 0.4 to 0.6 - 0.9. This can be related to the net effect of declining of evaporation of more volatile substances, textural changes due to the evaporation of substances from the texture and commencing of the evaporation of less volatile substances.

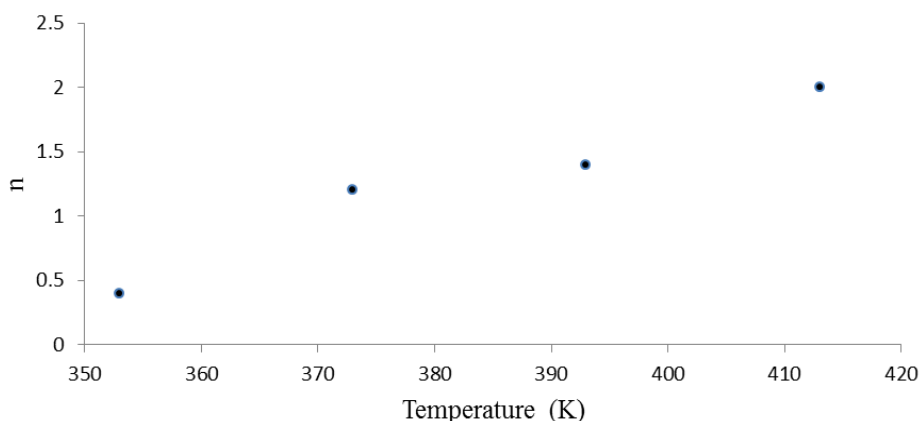


Figure 1- Variation of the power of the kinetic equation with absolute temperature

FTIR spectrums (Figure 3 and 4) of polypropylene sample after 14 hours period of time under the isothermal temperature at 80, 100, 120, 140 °C are almost same and comparable with original sample. It suggests that 14 hours period of time at these isothermal conditions are not sufficient for chemical changes of molecules.

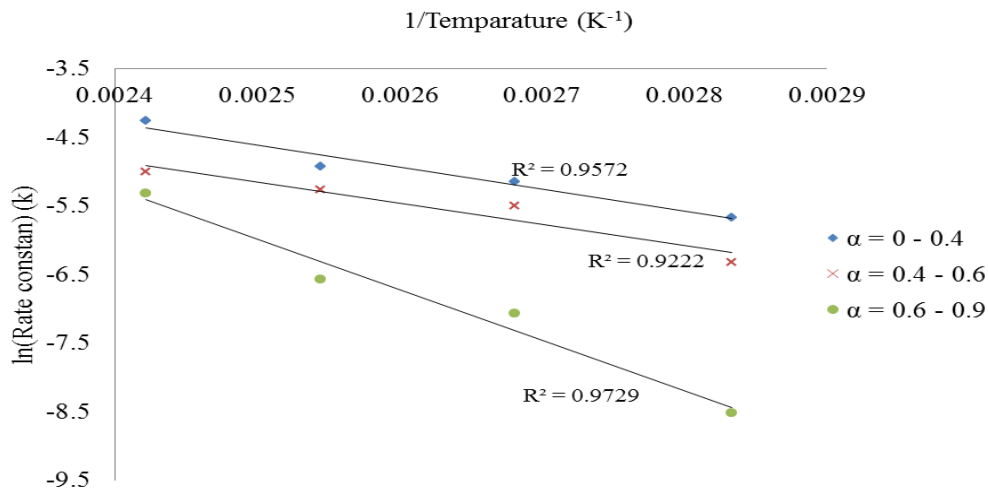


Figure 2- Variation of the  $\ln K$  with the reciprocal value of absolute temperature

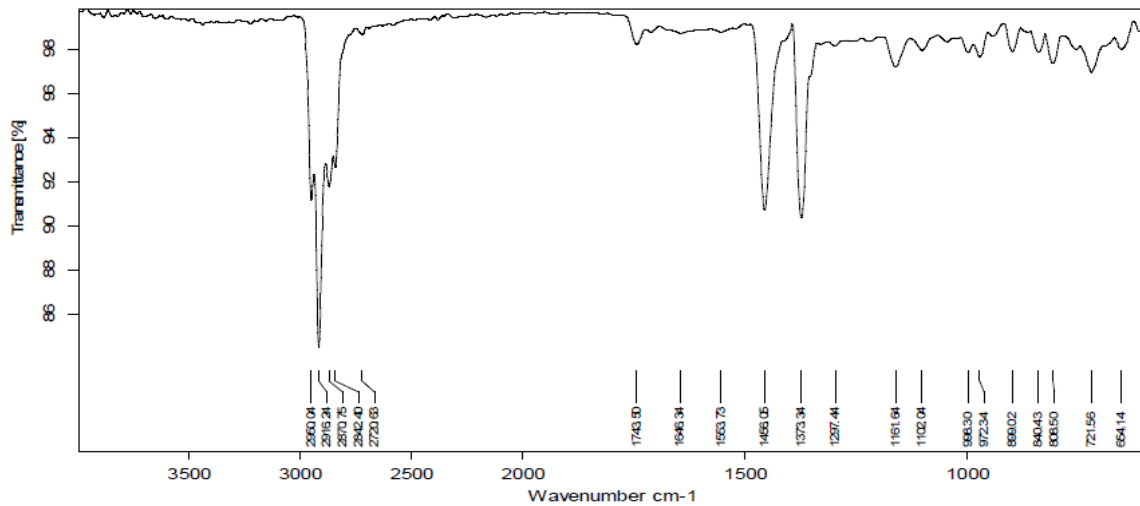


Figure 3- FTIR Spectrum of commercial PP before exposing to the thermal environment

Table 2 shows the effect of temperature on mechanical properties within the three different ranges of  $\alpha$ . Mechanical properties of samples at 0.4 of  $\alpha$  under the four different isothermal conditions are similar to the initial properties of samples. However, mechanical properties have significantly changed as the conversion reaches to 0.9. Tensile strength, braking strength and yield strength has increased by 31%, 35% and 10% respectively and strain at brake has decreased by 40% under the isothermal condition at 80°C. Changes of mechanical properties are significant even at low limit of  $\alpha$  to the 0.3% of weight loss below 100 °C.

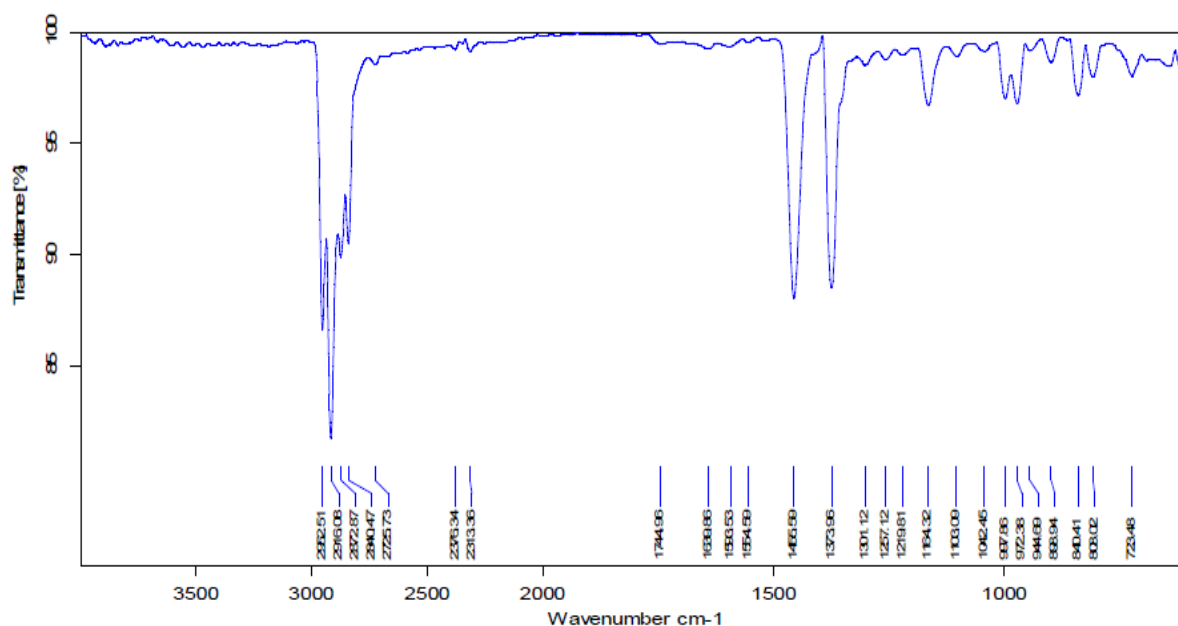


Figure 4- FTIR Spectrum of commercial PP after 14 hours at 140 °C.

Braking strength has decreased by 65%, 70.6% and 89% under the isothermal condition at 100 °C, 120°C and 140°C respectively. Weight loss due to the evaporation of more volatile substances has significantly increased the rigidity even at very low extent of weight loss.

Table 2- Mechanical properties at different isothermal conditions

<b>Conversion <math>\square = 0.4</math></b>				
	80°C	100°C	120°C	140°C
Tensile strength (MPa)	33.65	33.65	33.65	33.65
Braking strength (MPa)	28.85	28.85	28.85	28.75
Strain at brake	3.748	3.748	3.748	3.748
Yield strength(MPa) Elastic Limit (0.2)	32.65	32.65	32.65	32.65
<b>Conversion <math>\square = 0.6</math></b>				
Tensile strength (MPa)	41.5	43.15	54	48
Braking strength (MPa)	36.85	37.35	50.62	48
Strain at brake	3.08	3.04	1.71	0.6
Yield strength(MPa) Elastic Limit (0.2)	36	36	46	46
<b>Conversion <math>\square = 0.99</math></b>				
Tensile strength (MPa)	44	44	38	35.5
Braking strength (MPa)	39	43.4	37	35.5
Strain at brake	2.25	1.3	1.1	0.4
Yield strength(MPa) Elastic Limit (0.2)	36	42	37.5	35.5

#### IV. CONCLUSION

Kinetics of the weight loss of the waste polypropylene was studied under four different isothermal conditions. It was found 0.3%. Existing relationship in between activation energy and pre-exponential factor are function of the extent of conversion and temperature. Measurements of MFI and FTIR spectrums are not significantly change with the conversion of weight loss and hence change in weight loss is not mainly due to the degradation of polymer molecules. Rigidity has increased due to the loss of plasticizing effect of polypropylene products as a result of evaporation of more volatile substances. Even though small weight loss has led to highly changed of mechanical properties of polypropylene.

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