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Behaviour of order of reaction and toughness of polypropylene at artificial thermal condition

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Abstract: Polypropylene is accumulated in the environment that serious cause for society and human. It's degradation under artificial climate was studied in this research. Polypropylene pieces (3*15cm) were weighted and they were kept under artificial thermal condition for 0-12 hours at 80,100,120,140˚C temperature and weight were recorded at different time interval. Average weight loss of polypropylene samples were 0.3 – 0.4 % at end of 12 hours. The order of reaction (n) varies was obtained respect to degradation of polypropylene. The toughness of material was recorded, it varied from 35% to 95% from initial values.

Keywords: Polypropylene, Isothermal condition, Weight loss, Order of reaction

Introduction

Plastic has become an environmental problem since it is not properly disposed and takes significant percentage in solid waste / garbage. Polypropylene (PP) has been widely used as materials in the household appliance, medical equipment, automotive and other industries. Therefore, polypropylene has taken considerable amount in solid waste of plastic. The amount of accumulating polypropylene solid waste should be reduced by recycling or degradation. However, PP easily undergoes oxidative degradation under the influence of elevated temperature or sunlight, and the degradation leads to a deterioration of the mechanical properties (Madras & Bamtord, 2000). Since thermal degradation behavior of polypropylene is helpful to mitigate this waste accumulation problem and as well as this knowledge is important for recycling process to control the process parameter. Many kinetic models have been developed to describe kinetic degradation. These models were based on weight loss due to isothermal condition (Won, Sung & Seung, 2000).

In this study various models, such as; Kissinger, Fridman, Ozawa were applied to explain the thermal-degradation (Roy, Surekha, Rajagopal & Choudhary, 2007), and obtain the activity energy, frequency factor, and reaction order for the thermal degradation of each sample. Generally, the reaction rate of degradation is proportional to concentration of the reactant. In the case of polymer degradation it is usual to assume that the rate of conversion is proportional to the concentration of the material which remains to react. Meanwhile, the temperature dependence of the rate constant is given by Arrhenius expression (Huimin, Xiaoming & Edward, 2004). This paper is intended to initiate isothermal degradation studies of polypropylene and, obtained order of reaction and as well as toughness changed at different temperature.

Methodology

Commercial polypropylene samples, plastic boxes used in ice cream manufacturing industry with a medium density of 0.92g/cm3 were used as an investigating material. Dumbbell shape 0.2 mm thickness standard size samples were cut using cutting machine. The isothermal heating of polypropylene was

done at 80,100,120,140˚C various temperature. The weight of sample was reported at every two hour time interval from the beginning. Three replicate run of several representative samples and average value has been taken. There after data of experiment were analyzed. Using tensile test, tensile stress and tensile strain curves were obtained. There after toughens was calculated using tensile stress and tensile strain curves.

Kinetic model

The overall rate of polymer degradation is commonly described by Equation (1) (Flynn, 1989 &

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

Roy, 2007).

Parameters of the above formula are as follows. α is the polymer conversion, *t* is the time, *T* is the temperature (K), *R* is the gas constant (8.3134 KJmol^{-1} K^{-1}), *A* is the pre-exponential factor (min^{-1}), *E* is the activation energy (KJmol^{-1}), and *n* is order of reaction. The deficiencies of such a model-based approach are well known. In addition to the difficulty of determining a unique reaction model, the degradation of polymers tends to demonstrate complex kinetics that cannot be described by the single equation throughout the whole temperature region. Theoretical conversion could be by integrated of above formula. Such as;

$$\left[\frac{1}{(1-\alpha)^{n-1}}\right] = \left[(n-1)Ae^{-\frac{E}{RT}}t + 1\right] \dots\dots\dots \quad (2)$$

t = time (min)

where ; t = time (min)

Using integrated vision of Arrhenius equation and it was arranged *(y= mx +c)* (Ahmad , 2001).

$$\left[\frac{1}{(1-\alpha)^{n-1}}\right] = \left[(n-1)Ae^{-\frac{E}{RT}}t + 1\right]$$

y = m x + c

According to above equation gradient, *m* = slop of graph = $(n-1)Ae^{-\frac{E}{RT}}$

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Results and Discussion

Figure 1 shows behavior of weight reduction of polypropylene plastic material with time at different temperate. Rate of weight loss was initially high and with time it also reduced. Order of reaction *n* values were obtained by through graph and fit the liner equation *(y= mx +c)*. Interpreted both graph sets are shown in below Figure 1. Correlation *(r)* of graphs is nearly 0.96. Weight loss of polypropylene at each temperature is shown in Table 1.

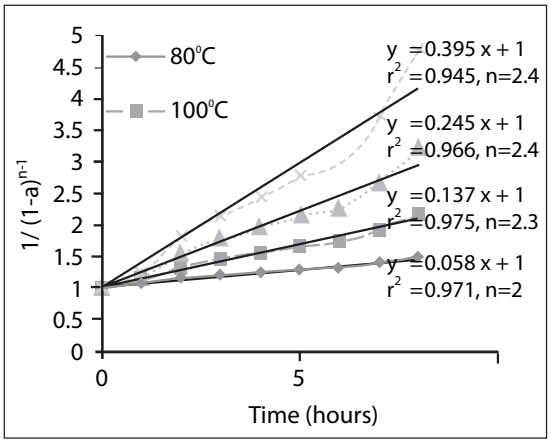

Figure 1:
Weight loss of polypropylene vs Time

Table 1:
Weight loss at different temperature for after 12 hours.

Temperature (˚C)	Percentage weight loss
80˚C	0.30
100˚C	0.33
120˚C	0.38
140˚C	0.40

Since existing mathematical model was suitable to predict order of reaction for polypropylene with respect to some specific values of n. Order of reaction n was 2, 2.3, 2.4, 2.5 with respect to 80˚C,100˚C,120˚C,140˚C temperature. Since order of reaction can be predicted by using Arrhenius model and other two parameters can be calculated by using differentiation. Order of reaction of Isothermal degradation of polypropylene plastic can be predicted by utilizing weight loss vs time curve. This method cannot be used to predict level of degradation for natural accumulated polypropylene since initial weigh of plastic sample and manufacture date are also unknown.

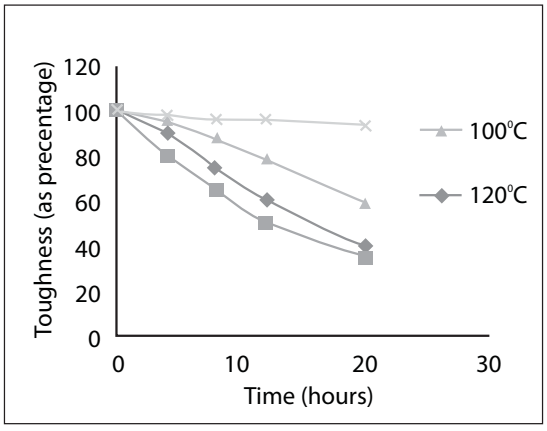

Figure 2:
Behavior of toughness vs Time

Figure 2 is shown behavior of toughness of polypropylene *vs* time at different temperature. (80˚C 100˚C, 120˚C, 140˚C).

Table 02:
Toughness at different temperature for after 20 hours.

Temperature (˚C)	Percentage toughness value reduction from initial value
80˚C	95
100˚C	60
120˚C	40
140˚C	35

Table 2 is indicated toughness values have at 100˚C, 120˚C, 140˚C after 20 hours. Toughness values were rapidly reduced above manner and it shows some aspects of isothermal degradation.

Conclusions

Polypropylene 0.3-0.4% average weight loss was apparent from 80˚C to 140˚C temperature for after 12 hours. The toughness variations were very significant from 80˚C to 140˚C temperature and it shows isothermal degradation has started. Using Arrhenius formula order of reaction (***n***) can be predicted, and level of isothermal degradation can also be predicted, if initial weight was known.

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