Rheological and kinetic studies of low density polyethylene (LDPE) – chitosan biocomposite film

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Abstract. The amount of plastic waste has always increased over the years and caused many problems in the environment because of its poor degradation rate characteristics. Recently, the interest in biodegradable polymer to substitute these synthetic plastic materials has been increased. Biocomposite materials have better biodegradability rate and can be utilized for several applications, such as packaging, agriculture, biomedical and healthcare. Chitosan as natural polymer that has good biodegradability can be combined with low density polyethylene (LDPE) to improve its mechanical properties. The LDPE-chitosan biocomposites were made by mixing chitosan and LDPE with maleic anhydride as compatibilizer and perbutyl Z as an initiator. In this study, the decomposition kinetic and thermal behavior of low density polyethylene (LDPE)–chitosan biocomposites were investigated by thermogravimetric analysis (TGA). The residual weight of biocomposites after decomposition process was analyzed. The samples were heated in the range of temperature from 25 °C to 500 °C and at different heating rates of 5, 10, 15, 20 °C/min, respectively. The result shows that activation energy decreased along with the increasing of chitosan concentration. This result indicates that the LDPE-chitosan biocomposite is a promising candidate for substitution of synthetic plastic.

1. Introduction
Polyethylene is a synthetic polymer which widely used for various application, such as packaging materials, healthcare, agriculture, etc due to its versatility and low production cost [1][2]. However, polyethylene is not environmentally friendly because it takes several years to be completely degraded [3][4]. In the last decade, the development of synthetic-natural polymer has attracted much attention in order to increase its degradability [5][6].

Natural polymers such as collagen, chitosan, and starch are potential to be used as blending materials because of their biocompatibility and biodegradability [7]. However, it is still difficult to blend synthetic polymer with natural polymer because of their immiscibility [8]. Mir, et.al [8] tried to solve those problems by adding vinyl triethoxysilane (VTES) into chitosan-High Density Polyethylene (HDPE) films. The thermal, mechanical, rheological and morphological properties of the blends were analyzed. Another study was also conducted by Araujo, J.R. et. al [9] with addition maleic anhydride as coupling agent into HDPE-natural fibers blend. Then, they studied the thermal properties of the obtained blends.

Although there were some researchers reporting about thermal behavior of natural-synthetic polymer blend, none of them was studying the kinetic model. Therefore, we observed a kinetic model of
thermal degradation to get the kinetic parameters. In order to get the data, analysis was conducted using thermogravimetric (TG) and differential thermal analysis (DTA) simultaneously. The data could be used to measure the composition of blend, order of reaction, kinetic constants, and degradation steps [10].

This work was conducted to observe the thermal degradation’s characteristics of polyethylene-chitosan composites compared to polyethylene and evaluated the kinetic model of its thermal degradation.

2. Methods

2.1. Materials
Low density polyethylene (LDPE) was supplied by Petrochemia Plock (Poland) and local chitosan powder was purchased from PT Biotech Surindo (Cirebon, Indonesia). The properties of local chitosan powder as follow: deacylation degree >90 %, 10-500 cps viscosity, <1.5 % ash content, and protein content value <0.5 %. Commercial Maleic Anhydride was obtained from Sigma Aldrich Chemical Company, and Tert-butyl peroxybenzoate was purchased from NOF Corporation (Tokyo, Japan).

2.2. Film Preparation
The preparation of LDPE-chitosan blends was conducted by mixing and hot pressing processes. First, LDPE (70 % wt) was melted in labo plastomill at constant temperature 160 °C with the speed of mixing 50rpm. After LDPE melted, chitosan (30 % wt), malaic anhydride (4 % wt based on LDPE weight) and perbutyl Z (0.25 % wt based on LDPE weight) were added simultaneously into the labo plastomill and mixed at the same condition until the homogeneous mixture was obtained. The mixture was hot pressed at 40 kgt/cm² to obtain 0.5 mm of film thickness.

2.3. Thermal Analysis
Thermogravimetric (TG) and Differential Thermal Analysis (DTA) were conducted using TG/DTA Perkins Diamond Series. 5 mg of sample was put in an open pan and heated up to 1000 °C with variation of heating rate 5, 10, 15, and 20 °C/min, respectively.

2.4 Kinetic Modeling
For non-isothermal experiment, the reaction rate \( \frac{da}{dt} \) is proportional to the conversion and the kinetic constant as shown in (1):

\[
\frac{da}{dt} = k(T) f(\alpha) \tag{1}
\]

In this case, \( k(T) \), \( f(\alpha) \), \( t \), and \( \alpha \) are kinetic constant as function of absolute temperature, the function of conversion over time, time, and conversion, respectively.

In this study we use two kinetic models, Flyn-Wall-Ozawa method (FWO) [11] and Kissinger-Akahira-Sunose method (KAS) [12]. Activation energy (E) and Arrhenius constant (A), were estimated by assumption that the reaction is first order, and heating rate \( \frac{dT}{dt} \) is constant (\( \beta \)). The FWO method’s equation and KAS method’s equations can be modified as in equations 2 and 3, respectively.

\[
\alpha = 1 - \exp \left( -\frac{0.084AE}{RB} \exp \left( -1.0516 \frac{E}{RT} \right) \right) \tag{2}
\]

\[
\alpha = 1 - \exp \left( -\frac{ART^2}{EB} \exp \left( -\frac{E}{RT} \right) \right) \tag{3}
\]
3. Results and Discussion

3.1. Thermogravimetric Study
This study is conducted to analyze the thermal stability and thermal properties of LDPE and blend [10]. The weight loss (TG) and the rate of weight loss (DTG) of LDPE and the blend under 20 °C/min heating rate are shown in figure 1. LDPE showed a single degradation step, while blend showed 3 degradation steps. This result was similar to previous experiments [6, 13]. The first step is attributed to drying step, which the volatile materials are loss. The second step shows the degradation of organic compounds in term of char formation [14]. While the third step is attributed to the degradation of LDPE as it can be compared between figure 1a and 1b. The difference in DTG peak was caused by the difference of heating rate [15]. The difference in DTG peak for 5, 10, and 15 °C/min heating rate is shown in figure 2, while for 20 °C/min heating rate is presented in figure 1. It can be seen that increasing in heating rate lead to increase degradation rate of LDPE and the second step of blend. The heating rate greatly affected the experimental result, especially in specimens that tend to undergo post crystallization or recrystallization [16]. Since chitosan is non-crystalline component [17], thus its thermal behavior is different with the LDPE in second step that related to the degradation of chitosan. From the study, the highest peak for LDPE degradation rate occurs during the heating rate of 20 °C/min. While the highest peak for the second step of blend occurs at the heating rate of 20 °C/min.

![Figure 1](image-url)

**Figure 1.** Degradation profile with 20°C/min heating rate of (a) LDPE and (b) blend
Figure 2. Combustion profile of (a) LDPE 5°C/min, (b) LDPE 10°C/min, (c) LDPE 15°C/min, (d) blend 5°C/min, (e) blend 10°C/min and (f) blend 15°C/min

3.2. Molecular Dynamic Results
Kinetic parameters of modified FWO (2) and KAS (3) methods are determined based on maximum coefficient of determination ($R^2$). For LDPE, it is calculated by one stage degradation as the degradation showed one single step of degradation. While for the blend, two step degradation is used in the calculation. Combination of the second step and third step degradation as one stage degradation is more favorable, so that the stage on consist of the first step, while stage two consist of the second and third step. The combination is necessary in order to simplify the model. The relationship between weight loss and temperature with heating rate 20 °C/min for FWO methods are shown in figure 3 with the obtained parameters are shown in table 1 and 2.
Figure 3. The relationship between weight loss and temperature with heating rate (a) 20°C/min LDPE, (b) blend stage 1 and (c) polyblend stage 2 for FWO method

Table 1. Kinetic parameter for FWO method

| Sample | Stage | Heating Rate, °C/min | $\Lambda$, 1/min | $E_a$, kJ/mole | $R^2$ |
|--------|-------|-----------------------|-----------------|----------------|-------|
| Blend  | 1     | 5                     | $1.6003\times10^5$ | 43.1011        | 0.9900 |
|        |       | 10                    | $1.2989\times10^3$ | 39.9972        | 0.9941 |
|        |       | 15                    | $3.7168\times10^3$ | 44.0486        | 0.9942 |
|        |       | 20                    | $6.0178\times10^3$ | 45.0091        | 0.9919 |
|        | 2     | 5                     | $1.0387\times10^3$ | 49.8421        | 0.9682 |
|        |       | 10                    | $1.6746\times10^3$ | 49.3572        | 0.9647 |
|        |       | 15                    | $3.4708\times10^3$ | 51.4471        | 0.9813 |
|        |       | 20                    | $3.1241\times10^3$ | 50.0610        | 0.9957 |
| LDPE   |       | 5                     | $2.6682\times10^6$ | 94.9821        | 0.9934 |
|        |       | 10                    | $2.9937\times10^6$ | 93.1634        | 0.9941 |
|        |       | 15                    | $3.3520\times10^6$ | 93.0112        | 0.9993 |
|        |       | 20                    | $6.7188\times10^6$ | 96.0530        | 0.9985 |
Table 2. Kinetic Parameter for KAS Method

| Sample | Stage | Heating Rate, °C/min | A, 1/min | Ea, kJ/mole | \( R^2 \) |
|--------|-------|----------------------|----------|-------------|----------|
| Blend  | 1     | 5                    | 3.2241×10^4 | 39.1421    | 0.990    |
|        |       | 10                   | 7.1755×10^4 | 39.1299    | 0.992    |
|        |       | 15                   | 8.3899×10^4 | 40.4529    | 0.994    |
|        |       | 20                   | 1.7722×10^4 | 42.0667    | 0.992    |
|        | 2     | 5                    | 3.9517×10^2 | 49.4209    | 0.954    |
|        |       | 10                   | 8.1166×10^2 | 50.3019    | 0.933    |
|        |       | 15                   | 8.6297×10^2 | 49.4981    | 0.983    |
|        |       | 20                   | 1.0193×10^3 | 49.3720    | 0.992    |
| LDPE   | 5     | 1.5494×10^6          | 91.9763   | 0.993      |
|        | 10    | 2.8019×10^6          | 93.9218   | 0.992      |
|        | 15    | 4.4204×10^6          | 94.9054   | 0.999      |
|        | 20    | 3.4341×10^6          | 91.9794   | 0.999      |

The result showed that addition of chitosan in LDPE tends to decrease the activation energy for both FWO and KAS methods. The addition of chitosan into the LDPE matrix strongly influenced the thermal behavior of the blend. The activation energy of the blend is lower than LDPE suggest that the polymer chain of chitosan were weaker, thus the blend is easily to break due to the depolymerization and degradation of cross-linked chitosan. While the use of parameters value depend on the heating rate as shown in table 3. The activation energy of LDPE varied between 93.0112 – 96.0530 kJ/mole for FWO method and 91.9763 – 94.9054 kJ/mole for KAS method. The activation energy of stage one was 39.9972 – 45.0091 kJ/mole for FWO method and 39.1299 – 42.0667 kJ/mole for KAS method, while the stage two was 49.3572 – 51.4471 kJ/mole for FWO method and 49.3720 – 50.3019 kJ/mole for KAS method. The E values obtained from the FWO and the KAS methods slightly different as the result of distinctive linear approximation to the temperature integral.

Table 3. Range of degradation stage in several heating rate

| Stage | 5 °C/min | 10 °C/min | 15°C/min | 20 °C/min |
|-------|----------|-----------|----------|-----------|
| 1     | 30 – 185 °C | 30 – 200 °C | 30 – 220 °C | 30 – 235 °C |
| 2     | 186 – 510 °C | 201 – 535 °C | 221 – 565 °C | 236 – 600 °C |

4. Conclusions

The homogeneous LDPE-chitosan biocomposite were successfully made by mixing both maleic anhydride as compatibilizer and perbutyl Z as an initiator. The decomposition kinetic and thermal behaviour of the obtained biocomposite assessed by thermogravimetric analysis showed that the addition of chitosan in LDPE tended to reduce the activation energy. The activation energy varies between 93.01 - 96.05 kJ/mol for FWO method and 91.98 - 94.91 kJ/mol for KAS method for LDPE only; while the activation energy of the biocomposites varies between 39.99 - 51.45 kJ/mol for FWO method and 39.14 - 50.30 kJ/mol for KAS method.
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