



Thermal Behavior and Kinetic of Degradation of PVA and PVA/CS/AL Blend

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Abstract

Studying thermal behavior, especially regarding the kinetics of the degradation of materials has attracted attention in this recent years because it can provide information about the stability of materials in various conditions and how the mechanism of material degradation. In this research, the thermal behavior and kinetics of thermal degradation of polyvinyl alcohol (PVA) and polyvinyl alcohol (PVA)/cassava starch (CS)/alkaline lignin (AL) with glycerol as a plasticizer were investigated and compared by the thermogravimetric analyzer. The test was carried out for samples under non-isothermal conditions in nitrogen at a single heating rate of 10 °C/min. The activation energies were calculated using Coats-Redfern, Broido, and Horowitz-Metzger methods. The results showed that PVA/o and PVA/CS/AL had four decomposition steps with the main degradation of PVA/o and PVA/CS/AL in the second and third decomposition steps. The first degradation of PVA/o and PVA/CS/AL occurred at 125 °C - 270 °C with a decomposed mass of 35.94%, and 135 °C - 250 °C with a decomposed mass of 31.84%, respectively. The second degradation of PVA/o and PVA/CS/AL was at 270 °C - 385 °C with a decomposed mass of 40.33% and 250 °C - 395 °C with a decomposed mass of 38.62%. The values of activation energies using Coats-Redfern, Broido, and Horowitz & Metzger methods of PVA/o were 57.08 KJ/mol, 64.82 KJ/mol, and 70.57 KJ/mol, respectively. The values of activation energies using Coats-Redfern, Broido, and Horowitz & Metzger methods of PVA/CS/AL were 74.49 KJ/mol, 82.17 KJ/mol, and 95.65 KJ/mol, respectively. The lower activation energy indicates that degradation reactions occur more easily. PVA/CS/AL has slightly better thermal stability than PVA/o.

Keywords : PVA, PVA/starch/lignin blends, thermal degradation, kinetic analysis

INTRODUCTION

Plastic is everywhere. Modern human life cannot be separated from the use of plastic, not only for food packaging but in various sectors of life such as construction, transportation, agriculture, medicine, pharmacy, industry, etc. Plastic is widely used because it is cheap, light, easy to find, and practical. On the other hand, plastics are considered pollution that harms the environment and threatens the ecosystem. It is necessary to properly handle plastic waste processing and start switching to replacing conventional plastics with bioplastics. The usage of bioplastics is one of the solutions to participate in protecting the environment and ecosystem.

According to European Bioplastics, plastic can be called bioplastic if it is bio-based, biodegradable, or has both of these properties. Biobased and biodegradable are different. Biobased indicates that material comes from biological natural sources, whether it is degradable or not. Meanwhile, biodegradable is a material that can be degraded due to microorganisms such as bacteria,

fungi, and algae, the source of material can be from nature or not. From that definition, non-biodegradable plastics such as polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), and polyamide (PA) from biobased material are also bioplastics. Polyglycolide (PGA), polylactic acid (PLA), polytrimethylene terephthalate (PTT), polybutylene adipate-co-terephthalate (PBAT) from fossil resources are also bioplastics because they are biodegradable (Rydz et al., 2018). This definition may not be understood by some people.

Various bioplastics are currently being developed, both biobased and biodegradable. One of the bioplastics that have been widely developed is polyvinyl alcohol (PVA) based biodegradable plastic. PVA is extensively used in packaging film, paper and textile industry, the medical sector, etc (Muppalaneni & Omidian, 2013; Rajeswari et al., 2020; Zanela et al., 2016).

PVA is a biodegradable synthetic plastic that has attractive properties such as non-toxic, good transparency, biocompatible, and water-soluble (Wang et al., 2018). The molecular weight and degree of hydrolysis of PVA greatly affect its properties (Muppalaneni & Omidian, 2013). PVA also has limitations, mainly in thermal properties. It is complicated to make a film using the melt compounding method, whereas this method is cheaper than the solution method (casting) ((Rajeswari et al., 2020). Many strategies have been done to improve processabilities, such as the addition of plasticizers, crosslinker agent, and nanofiller (Kapoor, 2014; Mohsin et al., 2011; Taghizadeh & Sabouri, 2013; Zanela et al., 2016). Unfortunately, research rarely studies thermal behavior and kinetics of thermal degradation of PVA and PVA blends.

Thermal behavior and kinetic of thermal degradation can be studied through a thermogravimetric analyzer (TGA). TGA is a common thermal analysis technique that shows a mass decrease due to heating (Sedaghat et al., 2017). The sample is heated from room temperature until its exhaustive decomposition. Weight loss of material due to the heating process is monitored and recorded. The graph of TGA shows weight loss versus time and or temperature. The conversion (α) and decomposition stage can be obtained from this data.

In this work, we investigated and compared thermal behavior and kinetic of thermal degradation PVA and PVA/CS/AL through a thermogravimetric analyzer under non-isothermal conditions in a single heating rate. The thermal degradation process was studied using the calculation of activation energy using the Coats-Redfern, Broido, and Horowitz-Metzger methods.

METHODS

Materials

The material used in this study is the same as previous research (Ratnawati et al., 2022). polyvinyl alcohol (PVA) was Poval JP-18. Cassava starch (CS) was from PT. Budi Acid. Alkaline lignin (AL) was from Tokyo Chemical Industry, Co. Ltd. Plasticizer used Glycerol (GL) was technical grade from a local supplier.

Methods

Bioplastics, namely: PVA/o and PVA/CS/AL, were prepared with the melt compounding method according to a previous study (Ratnawati et al., 2022). The dried Polyvinyl Alcohol (PVA), Cassava Starch (CS), and Alkaline lignin (AL) with the composition according to Table 1. was mixed until homogeneous.

Table 1. Composition and Processing Condition of Bioplastics

Sample	PVA/CS (%)	AL (%)	*GL (%)
PVA/o	0	0	45.1
PVA/CS/AL	60 /40	10	45.1

*based on the weight percent of PVA/starch

Glycerol (GL) was added to blends and further mixed to obtain uniform blends. The blends were conditioned in the oven at 50°C for 24 hours before they were compounded using a Haake Rheomix 3000P Internal Mixer with a temperature of 197.6 °C, and a rotation speed of 100 rpm. The

compounded mixture was then extruded using a hot press molding machine (Toyoseiki Mini Test Press-10) at 180 °C and 100 MPa for 20 minutes. The Formed bioplastics were tested for thermal stability and degradation behavior using a Thermogravimetric analyzer (TGA).

Analysis

The thermal degradation behavior was determined using the thermogravimetric analyzer Mettler Toledo type TGA / SDTA 851. The testing parameters followed the previous study (Bhat et al., 2013). Samples of 10 mg were heated from room temperature to 500 °C with a heating rate of 10°C/min using nitrogen with a flow rate of 20 mL/minute. From the data obtained, the % decomposed mass is calculated as follows:

$$\% \text{ decomposed mass} = \frac{(W_0 - W_t)}{(W_0)} \times 100 \quad (1)$$

Where W_0 is the initial mass, and W_t is the mass at a certain time on heating (Bhat et al., 2013; Rani et al., 2021; Sedaghat et al., 2017; Zhou et al., 2009)

Kinetic Study of Degradation

The weight loss data of samples were collected and used to evaluate the kinetic of degradation. Activation energies were evaluated by Coats-Redfern, Broido, and Horowitz-Metzger methods. The final equations of those methods were shown in Table 2 (Kulkarni et al., 2019; Rani et al., 2021).

Table 2. Single heating rate kinetic methods for activation energy calculation

Methods	Equation
Coats-Redfern	$\ln \left[\frac{-\ln(1 - \alpha)}{T^2} \right] = \ln \left[\frac{AR}{BEa} \right] - \frac{Ea}{RT}$
Broido	$\ln \left[\ln \frac{1}{y} \right] = \left[\frac{Ea}{R} \right] \frac{1}{T} + C$
Horowitz-Metzger	$\ln (-\ln(1 - \alpha)) = \frac{Ea \theta}{R Ts}$

RESULTS AND DISCUSSION

Thermogravimetric and Differential Thermogravimetric Analysis

The thermogram for PVA/CS/AL and PVA/o samples can be seen in Figure 1. It is observed in Figure 1 that the remaining mass at the end of the test for the PVA/CS/AL sample is larger by about 9.11% than the PVA/o. The percentage of remaining mass at the end of the test for PVA/CS/AL and PVA/o was 15.01% and 5.9%, respectively. Bioplastic containing starch and lignin has better thermal stability than bioplastics containing only PVA. These results are in agreement with previous studies. The addition of lignin will increase the thermal stability of the material (Bhat et al., 2013; de Miranda et al., 2015; Kaewtatip & Thongmee, 2013). The addition of starch in PVA can improve thermal stability (Zhou et al., 2009). Further analysis using derivative thermogravimetric analysis shows that both samples went through 4 steps of weight reduction. The first step was between temperatures 40 – 125 °C for PVA/CS and 40 – 135 °C for PVA/CS/AL which correlate with water evaporation. The second step was between temperatures of 125 – 270 °C for PVA/CS and 135 - 250 °C for PVA/CS/. The third step was between temperatures of 270 – 390 °C for PVA/CS and 250 – 395 °C for PVA/CS/AL. The final step was between a temperature of 390-500 °C for PVA/CS samples and 395 – 500 °C for PVA/CS/AL. For more complete information, can be seen in Table 3.

Temperature range and weight loss at each decomposition step are presented in Table 3. In the first decomposition step, it can be seen that the PVA/o sample lost about 6.82% in weight, while the PVA/CS/AL sample had a higher weight loss, namely: around 7.97%. This is related to the water content in the two samples. In the second decomposition step, where the initial degradation occurs. The PVA/o sample lost about 35.94% in weight and the PVA/CS/AL sample lost 31.84%. In the third

and fourth decomposition steps, loss mass was respectively 40.33% and 11.01% for the PVA/o sample and 38.62% and 6.56% for the PVA/CS/AL sample. Until the end of the test, the weight loss for the PVA/o and PVA/CS/AL samples was 93.93% and 85.85%, respectively. The residue for the PVA/CS/AL sample was 15.01%, greater than the residue for the PVA/o sample, which was only 5.90%.

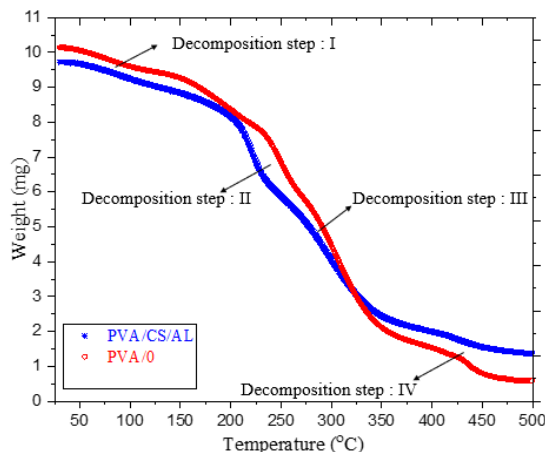


Figure 1. Thermogravimetric curves of PVA/o and PVA/CS/AL

Table 3. TG/DTG data of PVA/o and PVA/CS/AL at a heating rate of 10°C/minute

Sample	Decomposition step	T Range (°C)	Weight loss (%)
PVA/o	I	40-125	6.82
	II	125-270	35.94
	III	270-385	40.33
	IV	385-500	11.01
PVA/CS/AL	I	40 - 135	7.97
	II	135-250	31.84
	III	250-395	38.62
	IV	395-500	6.56

A larger residue indicates that the PVA/CS/AL sample has better thermal stability than the PVA/o sample. These results are following several previous studies. The addition of lignin and starch can increase the thermal stability of PVA. Taghizadeh et al. showed that PVA/Starch blend has lower thermal stability than pure starch (Sedaghat et al., 2017; Taghizadeh & Abdollahi, 2015). Zhou et al. also showed attested that the addition of starch can improve the thermal stability of PVA (Zhou et al., 2009). Bhat et al. studied incorporating lignin into Sago starch-based food packaging film. This study result showed that lignin could improve the thermal stability of starch-based film (Bhat et al., 2013). Korbag et al. studied the thermal properties of PVA/Lignin blends. The TGA result proved that the thermal stability of composite film slightly increased when lignin was added to PVA (Korbag et al., 2018). Wulandari et al. also showed that the incorporation of lignin in the starch/PVA blend can improve the thermal properties of the composite (Wulandari & Ratnawati, 2019).

The main degradation of PVA/o and PVA/CS/AL occurred in the second and third decomposition step (Table 3.). The first degradation started around 125 - 135 °C and finished around 250 - 270 °C. This is following Morancho et al. This study reported that the first degradation stage of PVA occurred from 130 to 260 °C. This stage was an elimination reaction that involve the elimination of side groups from the main chain and also the loss of water (Morancho et al., 2011). The second degradation took place from 250 - 270 °C to 385 - 395°C. This stage was further degradation involving the breaking of chain bonds and also the formation of low molecular weight compounds (Morancho et al., 2011).

Kinetic of degradation

The thermal degradation process can be estimated from activation energy. From the obtained data TGA under non-isothermal at a single heating rate can be calculated the activation energies using the Coats-Redfern, Broido, and Horowitz & Metger methods.

The calculation of activation energy using the Coats-Redfern method is presented in equation (2).

$$\ln \left[\frac{-\ln(1-\alpha)}{T^2} \right] = \ln \left[\frac{AR}{BEa} \right] - \frac{Ea}{RT} \quad (2)$$

Where α is a dimensionless conversion that is expressed as:

$$\alpha = \frac{m_0 - m}{m_0 - m_\infty} \quad (3)$$

where m_0 is the initial mass (mg), m is the mass at a certain temperature (mg), and m_∞ is the final mass (mg), T is the temperature (K), A is the pre-exponential factor (min^{-1}), Ea is the activation energy (KJ/mol), B is the heating rate (K/min) and R is the gas constant (8.314 J/K.mol). The activation energy (Ea) is obtained from the slope of the graph where $\ln \left[\frac{-\ln(1-\alpha)}{T^2} \right]$ as y-axis versus $\frac{1}{T}$ as x-axis.

The calculation of activation energy using the Broido method is presented in equation (4).

$$\ln \left[\ln \frac{1}{y} \right] = \left[\frac{Ea}{R} \right] \frac{1}{T} + C \quad (4)$$

Where y is undecomposed material ($1-\alpha$), T is the temperature (K), Ea is the activation energy (KJ/mol), R is the gas constant (8.314 J/K.mol), and C is constant. The activation energy (Ea) is obtained from the slope of the graph where $\ln \left[\ln \frac{1}{y} \right]$ as y-axis and $\frac{1}{T}$ as x-axis.

The calculation of activation energy using the Horowitz & Metger method is presented in equation (5).

$$\ln (-\ln(1 - \alpha)) = \frac{Ea \theta}{R T_s} \quad (5)$$

Where α is conversion, T_s is the DTG peak temperature (K), T is the temperature (K), θ is $T - T_s$, T is the temperature (K), Ea is the activation energy (KJ/mol), and R is the gas constant (8.314 J/K.mol). The activation energy (Ea) is obtained from the slope of the graph where $\ln (-\ln(1 - \alpha))$ as the y-axis and θ as the x-axis.

The calculation of activation energy at the first stage degradation using the Coats-Redfern, Broido, and Horowitz & Metger methods for PVA/o and PVA/CS/AL using equations listed in Table 2. is presented in Table 4., Figure 2., and Figure 3. The first degradation reactions in PVA and PVA blends were related to the elimination of side groups (hydroxyl groups) from the main chain (Morancho et al., 2011).

It is observed in Table 4., Figure 2., and Figure 3. that the value of activation energies using the Coats-Redfern, Broido, and Horowitz & Metger methods was consistent. PVA/o has slightly lower activation energy than PVA/CS/AL. The activation energy difference in both samples is approximately 17.35 – 25.08 KJ/mol. The lower activation energy indicates that degradation reactions occur more easily. This result is under previous studies. Taghizadeh et al. got a result that pure starch film has bigger activation energy than PVA/starch blend. Energy activation of pure starch film and PVA/starch blend was 158 KJ/mol or 160 KJ/mol, and 76 KJ/mol or 81 KJ/mol respectively (Taghizadeh & Abdollahi, 2015). Zhou et al. showed that the activation energy of PVA was lower around 40 KJ/mol than PVA/starch blends. The activation energy of PVA and PVA/starch blends was 127.3 and 167.7

kJ/mol, respectively. All data of activation energies using Coats-Redfern, Broido, and Horowitz & Metger methods shows a pretty good fit to a linear line with an R-squared value of more than 0.95.

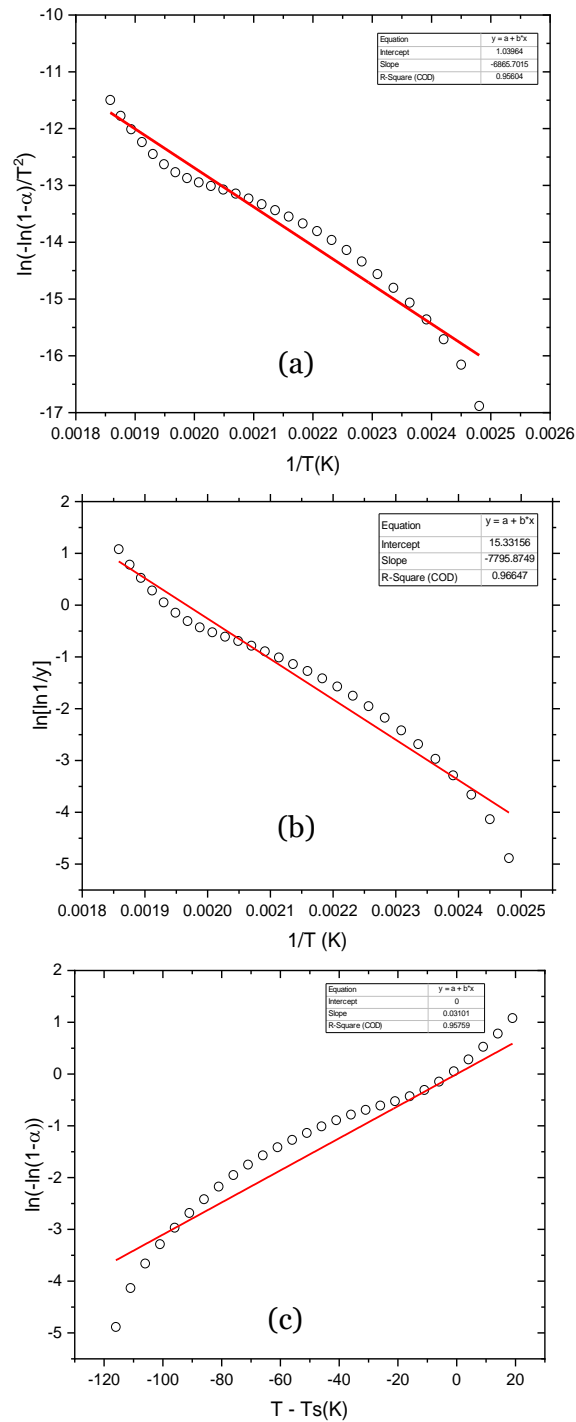


Figure 2. Activation energies of PVA/o obtained from (a) Coats-Redfern, (b) Broido, and (c) Horowitz & Metger plots

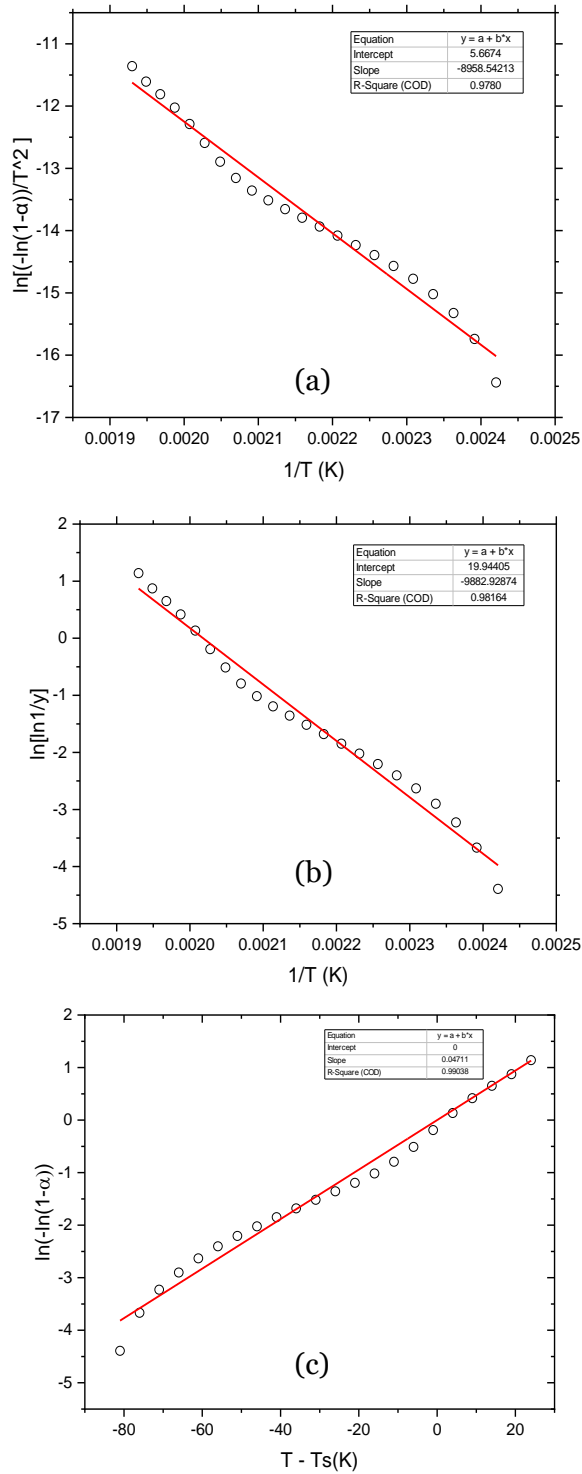


Figure 3. Activation energies of PVA/CS/AL obtained from (a) Coats-Redfern, (b) Broido, and (c) Horowitz & Metzger plot

Table 3. The activation energy of PVA/o and PVA/CS/AL

	PVA/o	PVA/CS/AL
Slope		
Coats-Redfern	-6865.70	-8958.54
Broido	-7795.87	-9882.93
Horowitz & Metzger	0.03101	0.04711
Activation Energy (KJ/mol)		
Coats-Redfern	57.08	74.49
Broido	64.82	82.17
Horowitz & Metzger	70.57	95.65
R-squared		
Coats-Redfern	0.95604	0.97800
Broido	0.96647	0.98164
Horowitz & Metzger	0.95759	0.99038

All three equations give a linear graph as shown in Figure 2 and Figure 3. The regression of all graphs is considerably good for a confidence level of 5%. The most accurate equation for PVA/o and PVA/AL/CS is according to Broido and Horowitz & Metzger approximation. The variations among the activation energies calculated by the three methods can be due to different approximations of the temperature integral whereas the deviation of a graph from a straight line can be caused by differences in initial weight observation due to unstable equipment or moisture content, and slightly different determination of the start and end of the reaction (Kulkarni, 2019).

The spread-out value of energy activation can be known from the standard deviation (σ) calculation. The standard deviation can be calculated using equation (6).

$$\sigma = \sqrt{\frac{\sum (Ea - \bar{Ea})^2}{N-1}} \quad (6)$$

where Σ is used to represent the sum, Ea is activation energy (KJ/mol), \bar{Ea} is average activation energy (KJ/mol) and N is the number of values in the sample.

The average activation energy for PVA/o and PVA/CS/AL is 64.16 KJ/mol with a standard deviation of 6.77 KJ/mol, and 84.10 KJ/mol with a standard deviation of 10.71 KJ/mol, respectively. This data is presented in Table 5.

Table 5. The standard deviation for PVA/o and PVA/CS/AL

PVA/o		
Ea	(Ea - \bar{Ea})	(Ea - \bar{Ea}) ²
57.08	-7.08	50.08
64.82	0.66	0.44
70.57	6.41	41.13
\bar{Ea}	64.16	Σ
σ	6.77	
PVA/CS/AL		
Ea	(Ea - \bar{Ea})	(Ea - \bar{Ea}) ²
74.49	-9.61	92.42
82.17	-1.93	3.74
95.65	11.55	133.33
\bar{Ea}	84.10	Σ
σ	10.71	

All methods for calculating activation energy from TGA data with a single heating rate are an approximation that has its limitation. The obtained values may not be the most accurate but can give an approximation range of the parameter.

CONCLUSION

Bioplastic of PVA/o and PVA/CS/AL with glycerol as a plasticizer was successfully produced by the melt compounding method. Thermal behavior was analyzed using TGA. Thermogravimetric analysis showed that both samples went through 4 decomposition steps. The first degradation process started around 125 - 135 °C and finished around 250 - 270 °C. The second degradation took place from 250 - 270 °C to 385 - 395°C. Kinetic degradation was studied with an approach using Coats-Redfern, Broido, and Horowitz & Metger methods. The calculation of energy activity using all 3 methods showed that PVA/o had a lower activation energy than PVA/CS/AL. It confirmed that the addition of starch and lignin in PVA can improve thermal stability PVA.

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