



THERMAL AND ACTIVATION ENERGY OF RENEWABLE POLYMER AFTER UV IRRADIATION

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ABSTRACT

Renewable polymer made from renewable material is one of the most important group of polymer because of their versatility and they can be manufactured in a wide range of insulation and automotive application. In this project, renewable polymer based on waste vegetable oil were synthesized and crosslink with commercial polymethane polyphenyl isocyanate. The renewable polymer foam was compressed by using hot compression moulding technique at 90 °C based on the evaporation of volatile matter and known as compressed renewable polymer (CRP). The thermal degradation and activation energy of CRP samples is consistent with the increasing of UV irradiation time at the first degradation, second degradation and third degradation. This is due to thermal stability of CRP samples at the hard segment has a great influence on the thermal stability of soft segment. The higher thermal stability of hard segment leads to a higher degradation temperature of soft segment.

Keywords: renewable polymer foam, UV irradiation, activation energy.

INTRODUCTION

Polyurethane (PU) foam are versatile engineering materials which find a wide range of applications because of their properties can be readily tailored to form different types of polymer composition. Generally PU foams is one of the major production from urethane polymer structure (Hassan *et al.*, 2014). The formation of biopolymer foam is followed the same general reaction of isocyanate with bio-monomer and both of which are derived when polymerization reactions occur similar to nearly all polymeric materials (Lim *et al.*, 2008).

Waste vegetable based palm oils are most abundant biological sources and important raw materials for the production of bio-based polyurethanes. The main components existing in waste vegetable oil are triglycerides with saturated and unsaturated fatty acids useful in many synthesis transformations and become new polyol sources (Ronda *et al.*, 2011). In polymer industry, waste vegetable oils which represent a major potential source of chemicals have been utilized as an alternative feedstock for bio-monomers (Narine *et al.*, 2007; Rus *et al.*, 2008; Rus *et al.*, 2009; Hassan *et al.*, 2013).

Synthesis of bio-monomer is started with the preparation of catalyst to generate the epoxides from the unsaturated fatty compounds of the waste vegetable oil. The condensation process comprises of acid-catalysed ring-opening of the epoxides to form polyols.

Thermal gravimetric analysis (TGA) is an analytical technique that measures the decomposition weight loss of a small polymer sample as a function of time or temperature and hence gives a quantitative description of the thermal stability of material and the amount of the corresponding residue. The derivative weight loss curve known as differential thermo

gravimetric analysis (DTG) shown on the TGA thermogram can be used to understand the onset decomposition temperature, the temperature at which the rate maximum of decomposition and decomposition temperature as well as the number of step involved in the thermal degradation of polyurethane foam.

In general, the thermal degradation of polymer involved in the initial stage were trapped volatile material which were released. The next step is scission and depolymerization, resulting in weight loss and degradation of mechanical properties. Thermal degradation of polymer occurs in three stages in which stage I refers to initial degradation in primary the decomposition of the hard segment, stage II proceeds with the depolycondensation and polyol degradation mechanism and affected by the soft segment content and stage III is attributed to ash formation.

EXPERIMENTAL

Preparation of sample

The monomer conversions from waste vegetable oils are started with the in-house catalyst preparation to generate the epoxies from the unsaturated fatty compound. The acid-catalyst ring opening of the epoxides is to form polyols (Hassan *et al.*, 2013). The weights of compositions were determined based on ratio of monomer and isocyanate with ratio of 2:1. 160 g of renewable polymer foam was weight and filled in the mould cavity with internal core size of 180 x 180 x 15 mm in order to decrease the thickness and pore size. This is conducted by using hot compression moulding apparatus. The parameter of the compression machine was set at 90°C of



temperature, under 26 tonnes of pressure within 1 hour (Latif *et al.*, 2014) to produce the compressed renewable biopolymer (CRP) samples. CRP were irradiated to UV light in UV Lamp Test Chamber Model HD-703 (Haida International Equipment Co., LTD) at various irradiated time at 250 hours, 500 hours, 750 hours and 1000 hours at 50 °C to simulate harsh environmental weather condition.

Thermal gravimetric analysis (TGA)

Thermal gravimetric analysis (TGA) measurement of BF and BC was performed using *Linseis TGA* to characterize the thermal properties of samples according to ISO 11358. The weight loss and derivative weight loss was measured at 20 °C to 900 °C with heating rate of 10 °C/min under oxygen atmosphere and flow rate of 0.3 µL using alumina crucible. Furthermore, activation energy of CRP samples were determinate by using Flynn method.

RESULT AND DISCUSSIONS

Figure-1 and Figure-2 shows the major decomposition of CRP samples with UV irradiation exposure at the high temperature ranges 290°C to 510°C. This peak was attributed to hard segment of crosslinker as consequence of the relatively low thermal stability of the urethane groups. The degradation of CRP samples was depend on thermal stability of isocyanate content in which it are less thermal stable after UV irradiated. This is indicated by the decreasing of first weight loss of CRP samples at 0 hours and 250 hours UV irradiation for the first decomposition temperature at 253 °C and 248 °C and second decomposition temperature is at 411°C and 380 °C and third decomposition temperature is 584 °C and 564 °C, respectively. The duration times of UV irradiation exposure of CRP samples also affected the percentages of weight loss significantly. It indicated that irradiation of CRB samples occurs due to photo degradation of renewable polymer from the exposed CRP samples surface.

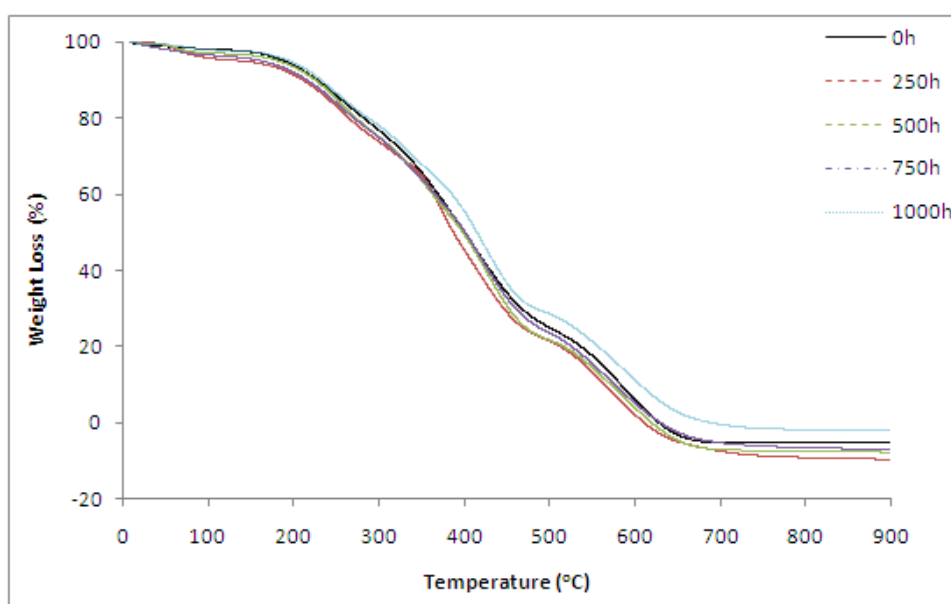


Figure-1. Thermogram weight loss of CRP samples with UV irradiation.

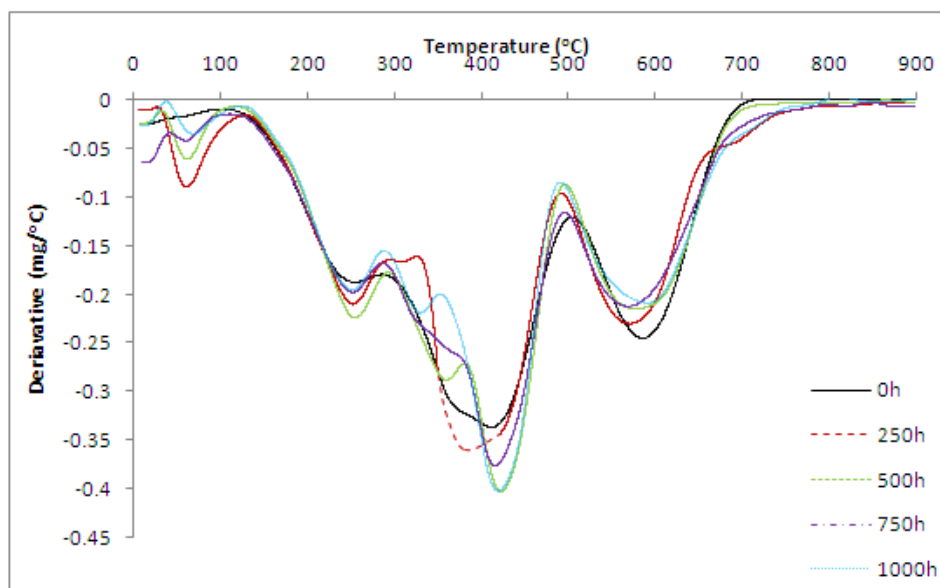


Figure-2. Thermogram derivative weight loss of CRP samples with UV irradiation.

Table-1. Thermal property of CRP samples with UV irradiation exposure.

CRP samples	UV irradiation exposure				
	0h	250 h	500 h	750 h	1000 h
Volatile (°C)		68	56	60	60
T _{on} (°C)		36	28	32	30
T _{max} (°C)		180	184	164	184
Weight loss (%)		5%	2%	3%	2%
1 st Decomposition (°C)	253	248	184	248	252
T _{on} (°C)	126	180	332	164	184
T _{max} (°C)	384	312	492	280	284
Weight loss (%)	20	22%	24%	22%	18%
2 nd Decomposition (°C)	411	380	420	416	420
T _{on} (°C)	384	312	332	280	284
T _{max} (°C)	508	460	492	494	484
Weight loss (%)	53%	48%	44%	52%	52%
3 rd Decomposition (°C)	584	564	576	572	588
T _{on} (°C)	508	460	492	494	484
T _{max} (°C)	679	660	650	650	668
Weight loss (%)	25%	25%	23%	23%	28%

Table-1 summarizes the percentages of derivative weight loss and decomposition temperature of CRP samples with UV irradiation exposure from 0 hours to 1000 hours. The CRP samples shows new existing of volatile peak less than 100°C is started with 250 hours UV irradiation exposure. This is due to formation of water soluble product in addition with volatile product at surface of CRP samples during exposed to UV irradiation. The weight loss of volatile material gives 5 % at 250 hours and leads to reduce of 2 % at 1000 hours. The first peak of

degradation of CRP samples with UV irradiation was started at around 120 °C to 290 °C, is attributed to the first decomposition of renewable polymer. However, the second decomposition was started from 290 °C to 510 °C due to the degradation of polymeric hard segment phase. Meanwhile, the third decomposition stage begun at 510 °C to 670 °C which is refer to soft segment of polymeric degradation temperature.



Kinetic analysis

The degradation process of CRP samples can be characterized by activation energy, measured with TGA experimental data using analytical method proposed by Flynn. This is due to mechanism changes during the degradation of renewable polymer; activation energy is not only a function of chemical structure of polymer but also varies with conversion. It provides a parameter for the assessment of thermal stability of renewable polymer.

Flynn method is applied to low conversion between 1 % and 5 % of nonisothermal differential weight loss (DTG) method with constant heating rate, Hr. In this study, the conversion rate α is defined as the degree of conversion (α) = weight loss at the given temperature (total weight loss of the degradation) respectively (Song *et al.*, 1999). The α is defined in equation (1).

$$\alpha = 1 - \frac{w(t)}{w_o} \quad (1)$$

w_o = initial weight,
 $w(t)$ = weight at any time,
 t = during degradation.

The fundamental rate equation in all kinetic studies is express as:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) = A \exp\left(\frac{-E_a}{RT}\right) f\alpha \quad (2)$$

k = rate constant,
 $f(\alpha)$ = reaction model, a function depending on the actual reaction mechanism.

For non-isothermal thermogravimetric analysis at constant heating rate, thus equation (2) may be written as equation (3) by using Flynn method.

$$\frac{d}{dt} \left[T^2 \frac{d\alpha}{dT} \right] = \frac{E_a}{T} + 2T \quad (3)$$

E_a = activation energy (kJ/mol),
 R = gas constant (8.314 J/K.mol),
 T = absolute temperature (K).

In this study, it is assumed that CRP samples are a first order reaction. Although it is not always the case, but the simplicity and the number of parameters of the first order model allow the direct comparison of different sample to provide preliminary parameter for further and more accurate modeling. In Flynn method $T^2 \left(\frac{d\alpha}{dt} \right)$ is plotted against α for series of experiment performed using TGA at 10°C/min heating rate with peak temperature obtained from the DTG curve.

Figure-3 show the activation energy of CRP samples of UV irradiation exposure from 0 hours to 1000 hours. The activation energy of CRP samples gives similar trend on range at the first decomposition temperature (1030-1050 kJ/mol), second decomposition temperature (1300-1390 kJ/mol) and third decomposition temperature (1670-1725 kJ/mol) respectively. This is due to thermal stability of CRP samples at the hard segment has a great influence on the thermal stability of soft segment.

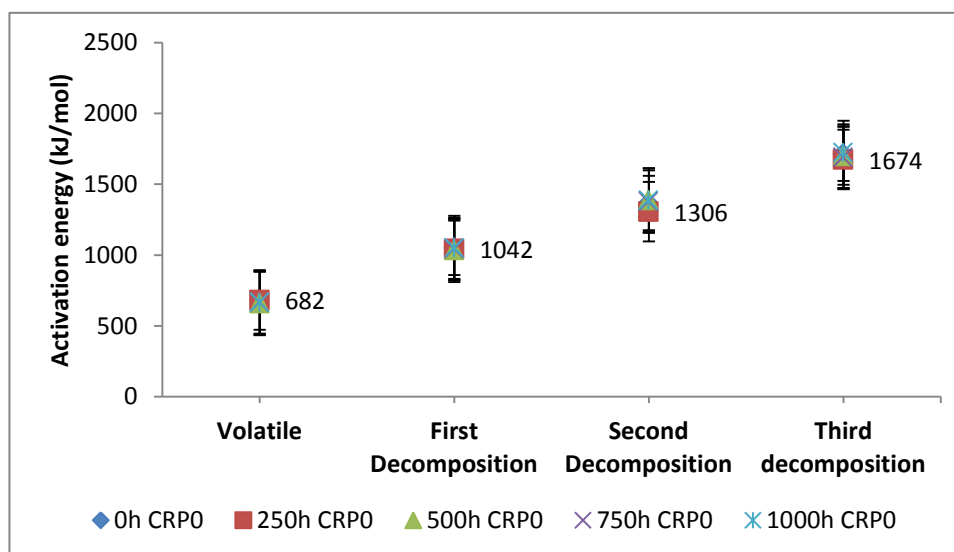


Figure-3. Activation energy of CRP samples of UV irradiation.



CONCLUSIONS

Compressed Renewable Biopolymer (CRP) is a renewable polymer based on waste vegetable oil is used to characterize the thermal degradation and activation energy after UV irradiation exposure. The thermal degradation and activation energy of CRP samples is consistent with increasing of UV irradiation time at the first degradation, second degradation and third degradation. This is due to thermal stability of CRP samples at the hard segment has a great influence on the thermal stability of soft segment.

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