Jurnal
Teknologi

Full Paper

THERMAL GRAVIMETRIC AND ACTIVATION ENERGY ANALYSIS OF RENEWABLE POLYMER UPON ULTRAVIOLET (UV) IRRADIATION

Nik Normunira Mat Hassan*, Anika Zafiah M. Rus

Sustainable Polymer Engineering, Advanced Manufacturing and Material Center (AMMC), Universiti Tun Hussein Onn Malaysia, 86400 Parit Raja, Batu Pahat, Johor

Article history
Received
15 July 2015
Received in revised form
1 October 2015
Accepted
25 October 2015

*Corresponding author
niknormunira@gmail.com

Graphical abstract

Abstract

Renewable polymer made from renewable material is one of the most important groups 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 (RPF) 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 RPF and CRP samples is consistant with the increasing of UV irradiation time at the first degradation, second degradation and third degradation. This is due to thermal stability of samples at the hard segment has a great influence on the thermal stability of soft segment. A higher thermal stability of hard segment leads to a higher degradation temperature of soft segment.

Keywords: Renewable polymer foam; UV irradiation; activation energy

Abstrak

Polimer yang boleh diperbaharui diperbuat daripada bahan yang boleh diperbaharui merupakan salah satu kumpulan yang paling penting dalam polimer kerana sifat fleksibilitinya dan digunakan sebagai penebat dan aplikasi automotif. Dalam projek ini, polimer boleh diperbaharui berasaskan minyak sayuran buangan telah disintesis dan sambung silang dengan komersial polymethane polyphenyl isosianat. Busa polimer yang boleh diperbaharui (RPF) telah dimampatkan dengan menggunakan teknik acuan mampatan panas pada 90 °C berdasarkan kepada penyejatan bahan yang tidak menentu dan dikenali sebagai polimer boleh diperbaharui yang dimampatkan (CRP). Degradasi dan tenaga bagi RPF dan CRP sampel adalah consistant dengan peningkatan masa penyinaran UV di degradasi pertama, degradasi kedua dan degradasi ketiga. Ini adalah kerana kestabilan terma sampel berlaku di segmen keras yang mempunyai pengaruh yang besar terhadap kestabilan haba pada segmen lembut. Kestabilan terma yang lebih tinggi oleh segmen keras membawa kepada pengurangan suhu yang lebih tinggi pada segmen lembut.

Kata kunci: Busa boleh diperbaharui; sinaran UV; tenaga pengaktifan

1.0 INTRODUCTION

Recently, natural vegetable oils are considered to be one of the most important classes of renewable source and have high potential to be synthesised and become a new polyol sources for polyurethane and can be replaced for commercial polyol in polyurethane manufacturing. The synthesis of polymeric materials from renewable recourses has been and remains until this date as one of the greatest challenges for the scientific community. Nowadays, considering the economical and environment concern, together with an increasing dependence on petroleum resources, have reinforced the need of using sustainable renewable resources.

The developing of renewable resources such as soybean oil, canola oil, rapseed oil, corn oil, palm oil, sunflower and linseed oil for polymer industries become highly desirable for both economic and environmental reasons [1]. Bio-polyol from vegetable oil which is non-petroleum based that is renewable, less costly and more eco-friendly was applied as an alternative to reduce the consumption of petroleum. Among the different natural oils, the vegetable oils from palm oil are widely explored for bio-polyol synthesis due to the main components existing in vegetable oils which are triglycerides. These triglycerides are available as platform chemicals for polymer synthesis. Several reactive positions of triglyceride vegetable oil which are saturated and unsaturated fatty acids are useful in many synthesis transformations and have become a new polyol source [2].

In particular polyol and it's crosslinker; isocyanate in which the solidify polymer known as polyurethane is mainly depends on the types of polyol such as functionality and hydroxyl value. Thus, the polyurethane elastomer which was successfully synthesized using vegetable oil derived from polyol revealed the improvement of thermal stability and oxidation resistance [3].

Waste vegetable-based palm oils are the most abundant biological sources and important raw materials for the production of bio-based polyurethanes. In polymer industry, waste vegetable oils which represent a major potential source of chemicals have been utilized as an alternative feedstock for bio-monomers [4-7].

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.

Meanwhile, polyurethane (PU) foams are versatile engineering materials which find a wide range of applications because their properties can be readily tailored to form different types of polymer composition. Generally PU foam is one of the major productions of the urethane polymer structure [8]. The formation of biopolymer foam is followed with 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 [9].

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 themogram 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 the polyurethane foam.

In general, initial stage of thermal degradation of polymer consist volatile material which was released during degradation. 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.

2.0 EXPERIMENTAL

2.1 Preparation Of Sample

The monomer conversions from waste vegetable oils were 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 [7]. The weights of the compositions were determined based on ratio of monomer and isocyanate with ratio of 2:1 to produce renewable polymer foam (RPF). 160 g of renewable polymer foam was weighted and filled in the mould cavity with an internal core size of 180 x 180 x 15 mm in order to decrease the thickness and pore size. This was 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 [10] to produce the compressed renewable biopolymer (CRP) samples as shown in Figure 1.

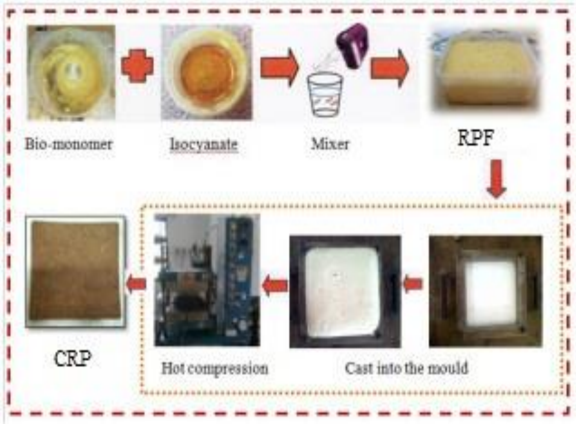

Figure 1 Fabrication of RPF and CRP

2.2 Artificial Weathering by UV Weatherometer

RPF and 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, 500, 750 and 1000 hrs at 50 °C to simulate harsh environmental weather condition.

2.3 Thermal Gravimetric Analysis (TGA)

Thermal gravimetric analysis (TGA) measurement of RPF and CRP was performed using *Linseis TGA* model 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.

2.4 Activation Energy

The activation energy of RPF and CRP samples was determined by using Flynn method. According to Flynn method the mechanism of polymer changes during the degradation and activation energy is not only a function of chemical structure of polymer.

3.0 RESULTS AND DISCUSSION

3.1 Thermal Degradation

The predetermined of UV irradiation temperature were based on weight loss curves (TG) and derivative thermo gravimetric (DTG) evaluation of RPF and CRP samples. The first peak appeared at the temperature range less than 100 ˚C due to the beginning of weight loss of volatile material [11-16] in the DTG evaluation profile of the samples. The first decomposition is tending to the first degradation of renewable polymer, second decomposition is second degradation of renewable polymer and third decomposition is attributed of third degradation of renewable polymer. The first peak of renewable polymer decomposition temperature correlates with the hard segment while the second peak correlates with the degradation of the soft segment. Qualitative characterization of the degradation process is elaborate by the onset and maximum peak temperature of the first step T_{1on} and T_{1max} along with the same for second step T_{2on} and T_{2max}. The detail of TGA onset decomposition temperature (T_{onset}) and the maximum decomposition temperature (T_{max}) for RPF and CRP samples are shown in Table 1.

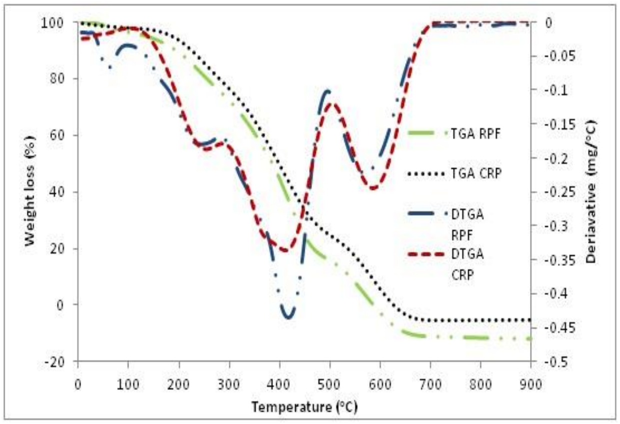

Figure 2 Thermogram (TG) and derivative weight loss (DTG) of RPF and CRP samples.

The onset degradation temperature T_{onset} and the maximum degradation rate temperature T_{1max} of the first RPF degradation stage are 238 °C and 419 °C respectively. Figure 2 shows the derivative weight loss of RPF and CRP was more than 94 % and 98 % respectively. The weight loss of RPF was started at less than 100 °C indicated as volatile matter in samples is equivalent to 4.3 %. It evidence that during fabrication of CRP samples by using hot compression moulding teachnique at 90 °C show was successfully removed the volatile matter. Therefore the setting temperature of hot compression moulding was selected as 90 °C.

The decomposition temperature is attributed to the crosslinker of flexible isocyanate content. It has been suggested the amount of weight loss at each degradation stage may used as a quantitative measurement of the hard and soft content in biopolymer. This is indicated by the first weight loss of RPF and CRP at almost the same for the first decomposition temperature at 238 °C and 253 °C and second decomposition temperature is at 419 °C and 410 °C respectively.

Table 1 Thermogram (TG) and derivative weight loss (DTG) of RPF and CRP samples

Samples	RPF	CRP
First Decomposition (°C)	238	253
T_{1on} (°C)	94	126
T_{1max} (°C)	283	384
Weight loss (%)	20	20
Second Decomposition (°C)	419	410
T_{2on} (°C)	283	384
T_{2max} (°C)	494	507
Weight loss (%)	57	53
Third Decomposition (°C)	567	584
T_{3on} (°C)	494	508
T_{3max} (°C)	678	679
Weight loss (%)	17	25

Figure 3 and Figure 4 show the major decomposition of CRP samples with UV irradiation exposure in 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 (crosslinker) 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 hr and 250 hrs 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 of CRP samples UV irradiation also affected the percentages of weight loss significantly. It indicated that irradiation of CRP samples occured due to photo degradation of biopolymer from the exposed CRP samples surface.

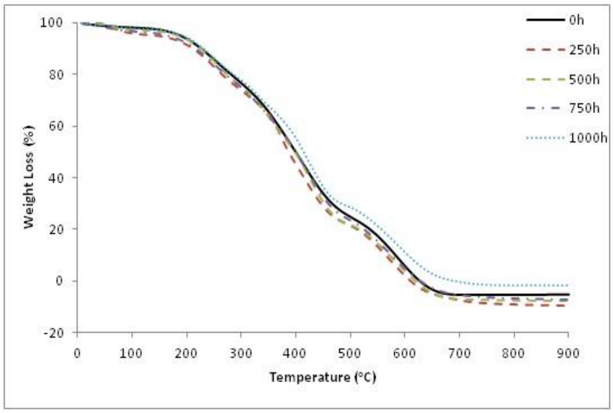

Figure 3 Thermogram weight loss of CRP samples with UV irradiation

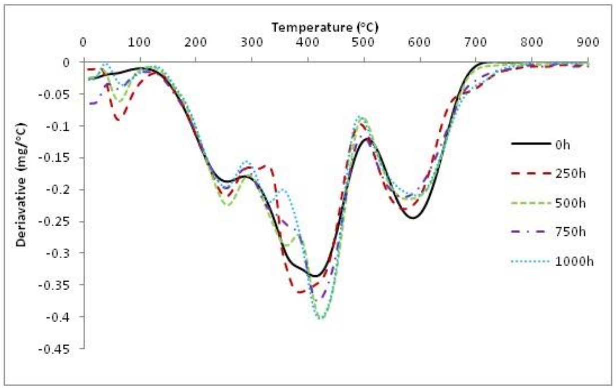

Figure 4 Thermogram DTG of CRP samples with UV irradiation

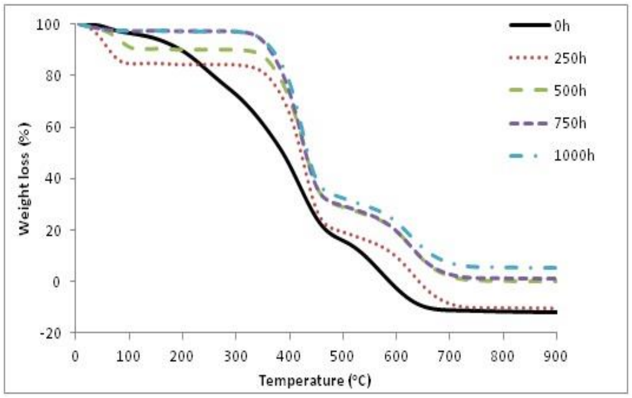

Figure 5 Thermogram weight loss of RPF samples with UV irradiation

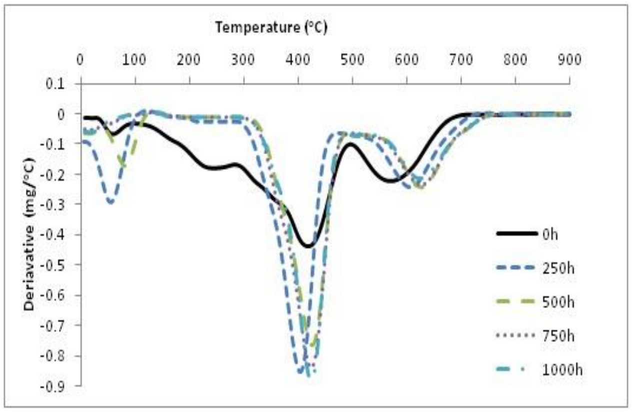

Figure 6 Thermogram DTG of RPF samples with UV irradiation

The thermal characteristic of RFP significantly changes after UV exposure are shown in Figure 5 and Figure 6. The thermal degradation of RPF was increased with increasing of UV exposure times. The first decomposition of RPF shows highest at 750 hrs after UV exposure is 436 °C and the weight loss is 71 % and was highest at the second decomposition is 626 °C and the weight loss is 27 % respectively. The volatile temperature was started eliminated at 750 hrs UV exposure.

Table 2 and Table 3 summarize the percentages of derivative weight loss and decomposition temperature of RPF and CRP samples with UV irradiation exposure from 0 hours to 1000 hrs. The CRP samples shows new existing of volatile peak less than 100 °C is started with 250 hrs 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 hrs and leads to reduce of 2 % at 1000 hrs. The first peak of degradation of CRP samples with UV irradiation was started from 120 °C to 290 °C, is attributed to the first decomposition of biopolymer. 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 referred to the soft segment of polymeric degradation temperature.

Table 2 Thermal property of CRP samples with UV irradiation exposure

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

Table 3 Thermal property of RPF samples with UV irradiation exposure

RPF samples	**UV irradiation exposure**				
	0 hrs	**250 hrs**	**500 hrs**	**750 hrs**	**1000 hrs**
Volatile (°C)	53	56	56		
T on (°C)	36	13	33		
Tmax (°C)	109	107	117		
Weight loss (%)	5	16	8		
1st Decomposition (°C)					
T on (°C)	238	428	428	436	424
Tmax (°C)	109	107	117	298	296
Weight loss (%)	290	464	295	481	484
	20	68	64	71	66
2nd Decomposition (°C)					
T on (°C)	419	620	622	624	629
Tmax (°C)	290	464	295	481	484
Weight loss (%)	501	709	489	742	744
	58	18	26	27	24
3rd Decomposition (°C)					
T on (°C)	567				
Tmax (°C)	501				
Weight loss (%)	717				
	17				

3.2 Kinetic Analysis

The degradation process of CRP and RPF 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 [17].The α is defined in equation (1).

$$\alpha = 1 - \frac{w(t)}{wo} \tag{1}$$

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

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

$$\frac{d\alpha}{dt} = k\ (T) f(\alpha) = A \exp(\frac{-Ea}{RT})\, f\alpha \tag{2}$$

k = rate constant
R = gas constant (8.314 J/K.mol)
f (α) = 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.

$$\frac{d}{dt}\left[T^2 \frac{d\alpha}{dT}\right] = \frac{Ea}{T} + 2T \tag{3}$$

E_a = activation energy (kJ/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 7 and Figure 8 show the activation energy of the RPF and CRP samples after UV irradiation exposure. The activation energy of RPF is similar at the volatile material and increased with increasing of UV exposure at first and second decomposition. For the third decomposition, the RPF does not have the activation energy. This is due to the RPF is successfully complete the decomposition after 250 hrs exposure to UV.

The activation energy of CRP samples gives similar trend of 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 of 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 whilst the activation energy of CRP samples is highest with higher thermal stability of CRP samples.

In comparison, the activation energy of CRP samples of UV irradiation of the volatile matter is less than 100 °C due to the volatile matter in CRP samples which has the least activation energy of UV irradiation. As the energy barrier, activation energy provides the information of critical energy needed to start the reaction. Thus to ensure lower activation energy, a lower temperature for photo stability of CRP samples is required.

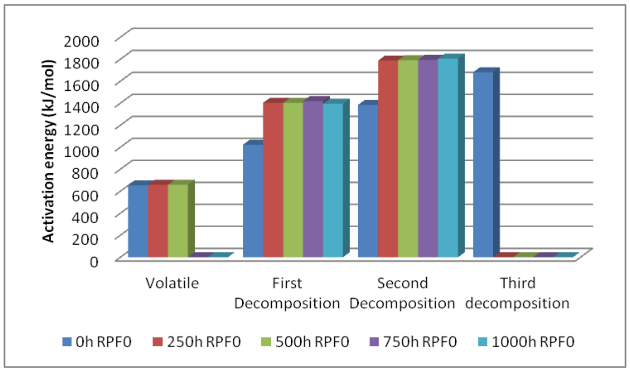

Figure 7 Activation energy of RPF samples of UV irradiation

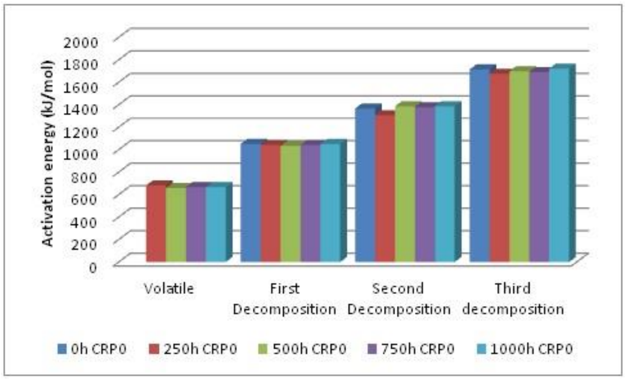

Figure 8 Activation energy of CRP samples of UV irradiation

4.0 CONCLUSION

Renewable Polymer Foam (RPF) and Compressed Renewable Polymer (CRP) are renewable polymer based on synthesis from waste vegetable oil. The characteristic of thermal degradation and activation energy after UV irradiation exposure were determined. The thermal degradation and activation energy of 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 samples at the hard segment has a great influence on the thermal stability of soft segment.

Acknowledgement

The authors would like to thank the Malaysian Government and Universiti Tun Hussein Onn Malaysia (UTHM), MyBrain15 Scholarship (MyPhd) and Malaysian Technical University Centre of Excellence (MTUN CoE) for supporting this research study under research grant Vot C014 and C015.

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