Thermal Characteristic of Biopolymer Foam using Hot Compression Technique

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Abstract. Flexible and rigid biopolymer foam were prepared by the reaction of polyol based on waste vegetable oil with commercial Polymethane Polyphenyl Isocyanate (Modified Polymeric-MDI) and Diisocyanate-diphenylmethane (MDI). The morphological study of flexible and rigid biopolymer foam were examined by Scanning Electron Microscope (SEM), Thermogravimetric analysis (TGA) and density. It was found that the density of flexible and rigid biopolymer foam was steadily increased after using hot compression moulding technique at 90°C. Furthermore, the flexible and rigid biopolymer foam gives a close cell structure and smallest cell size with hot compression technique which is 143.71 μ m and 90.01 μ m respectively. The thermal stability of rigid biopolymer foams exhibited the first degradation of hard segment occur at 276.32°C and the second degradation of soft segment at 421.05°C as compared to flexible biopolymer foam which is 238.39 °C and 419.44 °C, respectively. This behavior of thermal degradation of the hard segment and soft segment of biopolymer foam was changes after using hot compression moulding technique.

Introduction

Polyurethane (PU) foam are versatile engineering materials which find a wide range of applications because of their properties can be readily tailored by the type and composition of their component. However, the main market for PU foam is in polymeric foam, which are flexible and rigid [1]. Flexible and rigid PU foams are two predominant application forms of PU with coatings, sealants, elastomers, and adhesives being other common forms of applications. PU foam can be produced with open-cell structure to be more flexible or a close cell structure to be a more rigid [2]. Generally PU foams is one of major production from urethane material. The characteristic of PU foam can be changes via adjusting the chemical composition of the raw materials, in particular polyol and isocyanate in which the PU properties mainly depends on the types of polyol such as functionality and hydroxyl value [3].The bio-polyols synthesized from vegetable oils are attractive alternatives for produce green polymer foam. In polymer industry, vegetable oils which represent a major potential source of chemicals have been utilized as an alternative feedstock for bio-monomers [5-7].

Thermogravimetric analysis (TGA) is an analytical technique that measures the weight 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 thermogravimetric 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 flexible polyurethane foam. TGA is useful to determine thermal stability and degradation behavior of a polymer or composite [8].

Methodology

Materials. Biomonomer from waste vegetable oil, Polymethane Polyphenyl Isocyanate and Polymethane Polyphenyl Isocyanate (diisocyanate-diphenylmethane, MDI).

Foam Production. Biomonomer based on waste cooking oil from Small Medium Entrepreneur (SME's) was prepared by using in-house catalyst preparation to generate the epoxides from unsaturated fatty compound which comprises the acid-catalyst ring opening of the epoxides to form polyols [2-3,9]. The biomonomer is mixed with Modified Polymeric-MDI and diisocyanate-diphenylmethane (MDI) were prepared by simple open casting method to produce the biopolymer foam. The mixture was poured into open mould and allowed to rise freely and the biopolymer foam was removed from the mold after 12 hours.

Hot compression. 160g of biopolymer foam was weighted to fill into the mould with internal core size of $180 \times 180 \times 15$ mm to produce biopolymer foam after hot compression. The parameter of the compression machine was set at 90°C of temperature, under 26 tonnes of pressure within 1 hour. Two samples were prepared using this method based on rigid and flexible crosslinking agents.

Scanning Electron Microscope (SEM). The top surface of each green polymer foam samples was sputter coated with gold at 25mA plasma current and 2Pa of camber pressure to make them conducting. Cellular structure images were examined by using scanning electron microscope (SEM) of JEOL-JSM6380LA operates at 15kV at 30X magnification.

Thermogravimetric analysis (TGA). TGA measurement was performed using *Linseis TGA* for characterized the thermal properties of biopolymer foam. The TGA for flexible and rigid biopolymer foam was measured weight loss and derivative weight loss curve was heated in the thermal gravimetric furnace from 20°C to 900°C at the heating rate of 10° C/min under oxygen atmosphere, flow rate 0.3 µL and using alumina crucible.

Result and Discussion

Density of biopolymer foam

The density of rigid biopolymer foam gives largest as compared to flexible biopolymer foam before compression technique as refer on Figure 1. On the other hand, the densities of the biopolymer foam were changes significantly after compression technique at 90°C. According to X. Mao et al (2008) reported that the decreasing of the density was gives increasing of the cell size and window cell of foam [10].



Figure 1. Density of rigid and flexible biopolymer foam before and after compression technique.

Scanning Electron Microscope (SEM)

The cross section surfaces of rigid biopolymer foam of compressed and uncompressed technique were observed with SEM as shown in Figure 2 (a) and Figure 2(b). The shapes of the cells are spherical and close cell structure of rigid biopolymer. The cell structure is homogenous, small struts and lamellae before compression technique as shown in Figure 2(a). However, the morphology structure after compression technique gives non-homogenous and small struts as referred to Figure 2 (b). The average of cell size indicates that the highest cellular cell size is 501.5 μ m of uncompressed as compared to compressed technique sample is 90.1 μ m.



Figure 3. SEM micrograph of flexible biopolymer foam: (a) before compression and (b) after compress

The flexible biopolymer foam represent having open-cell cellular structure and anisotropic. According to Gibson & Ashby (1997) reported that almost all man-made foams are anisotropic [11]. The open-cell structure comprises many small open windows located on the cell wall and these cause the struts formed in between the open window [12]. The SEM results present the cell distribution of flexible biopolymer foam without compression technique shows uniform pore distribution, smaller cell size and homogenous. The larger cells were found without compression technique is 411.4 μ m as compare to cellular structure of the flexible biopolymer foam with compression technique is 143.71 μ m.

Thermogravimetric analysis (TGA)

Referring Figure 4, the first point degradation 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 TGA data, the onset decomposition temperature (T_{onset}) and the maximum decomposition temperature (T_{max}) for rigid and flexible biopolymer foam are shown in Table 1.



Figure 4. Thermogram of biopolymer foam (a) thermogravimetric (TG) and (b) Differential thermogravimetric (DTG)

The first peak of flexible biopolymer foam was appear at the temperature ranges less than 100°C due to the beginning of weight loss of volatile material in the DTG evaluation profile of the samples indicated in Figure 1 (b). It this sense, it has been reported that the first weight loss during thermal degradation of biopolymer foam at less 100°C due to the degradation of volatile material. The previous researchers was investigated the first peak of thermal degradation of biomass which is palm kernel shell, empty fruit brunch, palm mesocrap fiber and mukah baligian coal at the range of temperature less than 150°C due to the moisture drying stage. The thermal decomposition observed below 110°C corresponded to the moisture evolution of the water linked to the hydroxyl and carbonyl groups of the fiber. The maximum peak of biomass shows at 50°C probably moisture content of the samples [13].

Sample	First Decomposition Temperature (°C)	Second Decomposition Temperature (°C)	Third Decomposition Temperature (°C)
Rigid Biopolymer Foam	276.32 (0.19)	421.05 (0.537)	610.53 (0.895)
	$T_1 \text{ on} = 152.63$	$T_2 \text{ on} = 334.21$	$T_3 \text{ on} = 505.26$
	$T_1 \max = 334.21$	$T_2 \max = 505.26$	$T_3 \max = 742.11$
	Mass loss $= 0.242$	Mass loss $= 0.474$	Mass loss $= 0.242$
Rigid Biopolymer Foam	244.44 (0.153)	422.22 (0.505)	602.78 (0.857)
after compression	$T_1 \text{ on} = 138.89$	$T_2 \text{ on} = 338.89$	$T_3 \text{ on} = 516.67$
	$T_1 \max = 338.89$	$T_2 \max = 516.67$	$T_3 \max = 716.67$
	Mass loss $= 0.238$	Mass loss $= 0.448$	Mass loss $= 0.267$
Flexible Biopolymer	238.39 (0.168)	419.44 (0.632)	566.67 (0.947)
Foam	$T_1 \text{ on} = 94.44$	$T_2 \text{ on} = 283.33$	$T_3 \text{ on} = 494.44$
	$T_1 \max = 283.33$	$T_2 \max = 494.44$	$T_3 \max = 677.78$
	Mass loss $= 0.195$	Mass loss $= 0.574$	Mass loss $= 0.168$
Flexible Biopolymer	252.63 (0.152)	410.53 (0.562)	584.21 (0.914)
Foam after	$T_1 \text{ on} = 126.32$	$T_2 \text{ on} = 384.21$	$T_3 \text{ on} = 507.89$
compression	$T_1 \max = 384.21$	$T_2 \max = 507.89$	$T_3 \max = 678.95$
	Mass loss $= 0.2$	Mass loss $= 0.53$	Mass loss $= 0.25$

Table 1. Thermal decomposition of biopolymer foam

Table 1 summarized result of rigid and flexible biopolymer foam after compression moulding technique. The onset degradation temperature T_{onset} and the maximum degradation rate temperature T_{1max} of the first degradation stage of rigid biopolymer without compression technique are 276.32°C and 421.05°C, respectively as compared to flexible biopolymer foam which is 238.39 °C and 419.44 °C. The weight loss of rigid and flexible biopolymer foam were decrease from 0.19 to 0.153 for rigid and 0.168 to 0.152 for flexible biopolymer foam with compression technique. This behavior may due to the easy thermal degradation of the hard segment due to the amount of weight loss or percentages of mass loss in first stage decomposition was well correlated with the hard segment, suggesting that the degradation start in the hard segment [14].

Conclusion

The polyol based on waste vegetable oil could be used as one of the raw material for preparation of biopolymer foam. The overall density of biopolymer foam increased steadily and the morphology structure of cell size was decrease after compression moulding technique at 90°C. In addition, the thermal degradation of rigid biopolymer foam exhibited gives the highest hard segment and soft segment as compared to flexible bioploymer foam.

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