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THE EVALUATION OF RHEOLOGICAL PROPERTIES OF BIODEGRADABLE POLYLACTIC ACID BASED POLYURETHANES

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ABSTRACT

The project was expected to approach the synthesis of polyurethane polymerization process in two steps. First, the low molecular weight prepolymer of polylactic acid (PLA-OH) was synthesized via condensation polymerization of L-lactic acid (LA) Were prepared. The first stage of the synthesis, the pre-polymer chains linked together by diisocyanat HDI, Then in the second stage of the synthesis, using1,4-butanediol (the chain-extension) with high molecular weight polyurethane was prepared. This four different molar ratio of raw materials was

carried out, then the test FTIR, DTG, TGA, DSC, GPS, physical and rheological properties of polyurethane ratio parameters were evaluated and assessed on their properties out. The results showed a strong hydrogen bond between the rigid polyurethane obtained from aliphatic diisocyanate. The increase in percentage of hard segment, high heat resistance and good strength and elasticity polyurethane are associated with optimal properties.

Keywords: Rheological properties, polyurethane, poly lactic acid

INTRODUCTION

Important categories of biodegradable polymers are polyurethanes. Polyurethanes are a group of polymers that are prepared of a diisocyanate an extender chain and a polyol (eg polyester or polyether). Polyurethanes that are obtained from the reaction of these components indeed are the multi-block copolymers or partial polyurethane that are consist of polyurethane hard parts and polyester soft parts or polyether. The hard part acts as a amplifier fille and causes the dimensional stability of polyurethane and the soft section also gives it elastomeric properties [1]. A chemical and physical property of these polymers directly depends to the chemical percent composition of hard and soft parts, molecular weight and their ratio [2]. Biodegradable polyurethane are a bunch of polyurethane that in the preparation of them are used of polyols which are contain of biodegradable properties. For example, can be named from biodegradable polyurethane which are based on starch [3], PCL [4], esters of fatty acids [5] and also poly-lactic acid [6-7]. Diisocyanate be used in making of biodegradable polyurethane can be enter in reaction with polyol alcohol groups similar to making of conventional polyurethane and to have be followed the production of polyurethane groups or can act as a extender chain [7], which in this status the polyesters be used in making of polyurethane have been the polyesters with low molecular weight (pre-polymer) and

diisocyanate has acted as a chain extender and a polyurethane is provided with high molecular weight. Biodegradable polyurethane prepared on the basis of biocompatible poly-ester has been used and examined widely in biomedical applications. The point about this type of polyurethane that is important it's that despite of their good mechanical properties and biocompatibility that have, their molecular stability limit in the longer term in living tissues environment [8]. Poly (ester-urethanes) have wide applications as medical supplies. Degradation of these materials takes place through chemical hydrolysis or enzymatic in connection aliphatic ester of them. Stability against of hydrolytic poly (ether-urethanes) from poly (ester-urethanes) is more, but the poly (ether urethane) can be destroyed by oxidation and hydrolysis processes (which can be accelerated by enzymes [9]. Also, despite of this fact that restrictions on polyurethane molecular stability has caused problems in the making of body prosthetic by these materials, but extensive research have done in the field of making and development of biodegradable polyurethane [10]. As also mentioned above, biodegradability of poly (ester urethane) is carried out through degradation of ester groups available in the polymer main chain. One of the biodegradable polymers and biocompatible used as a building block in the preparation of biodegradable polyurethanes is poly lactic acid. Poly lactic acid is family member of aliphatic polyesters that initial research about it was focused more on properties and applications of poly-lactic acid biomedical.

MATERIALS

Consuming materials used for chemical reactionswere purchased from Merck company, Sigma and Saway with high purity percent that its specifications was brought up in Table 1.

Table 1: Consumables used in the synthesis of polyurethane

Molecular formula	Purity percent	density	dans	company	mixture
$C_8H_{12}N_2O_2$	99.999	168.2	1.047	merck	Hexa methylene diisocyanate (HDI)
HO-R-OH	99.999	500	-	sigma	Hydroxyl-terminated PLA (PLA-OH)
HO-(CH_2)OH	99.999	90	1.02	savay	1,4-butanediol

EXPERIMENTS

3.1. Prepare the reactor for the synthesis

For the synthesis of polyurethane based on poly-lactic acid hydroxylated beginning into oil bath was shed paraffin oil as thermal oil and its temperature was set on ℃ 120. Three-neck dirigible was attached to the clamp and was placed in paraffin oil bath, mixer moved into the balloon and its blade taken down until the mixture is well. The hose related to Nitrogen gas injection was attached from an balloon mouth and the gas flow was adjusted to the extent that the reaction be conducted without the presence of oxygen. The other mouth of the balloon where was materials entrance to the balloon to be blank by a stopper device. Since the final properties of the polyurethane is determined regarding to the molar ratios of participating materials, for this reason polyurethane was synthesized and studied with 4 different molar ratio of participating materials.

3.2. Synthesis of polyurethane

In this paper the polyurethane was synthesized with 4 different molar ratios of the participating materials and by the pre-polymer method, thus that beginning with the ration of amount first of 16/6 gr poly lactic acid hydroxylated melted inside of the balloons at 120℃, then the mixer was switched on and set with intensity of 100 rpm and amount of 11/16 gr diisocyanate added slowly during 5 minutes so that the foam is not created, before was established a mild stream of dry nitrogen gas in balloon until reaction is carried out without the presence of oxygen. Continued the rile continuous according to type of Isocyanate that to be used during 6 hr and finally reaction was terminated by

adding extender chain 1, 4 butane DL to amount 3 gr to pre-polymer obtained. After the uniform distribution of color in mixture that is complete mixing symptom of materials together, casting act the resulting mixture done in a clear aluminum container until is achieved one page to a 2 mm thickness .Then the aluminum container was placed in the vacuum oven at 120℃ and 24 hr until the polymerization reaction to be completed. The resulting pages were held at room temperature for at least two days and then were studied and examined. The synthesis of polyurethane with three other molar ratio done in the same way that was explained, so that the amount of poly-lactic acid hydroxylated in any fixed stage and amount of the isocyanate and Bhutan-DL that is include the percentage of the hard part % HS have increased and its impact on poly-Bhutan properties were studied. The related molar ratios have brought in Table 2.

Table 2 .molar ratio of participating materials in the synthesis of Polyurethane

Polyurethane	Molar ratio Polyol: HDI:1.4-BDo	% HS
PU-1	1:2:1	18
PU-2	1:3:2	25
PU-3	1:4:3	32
PU-4	1:5:4	39

RESULTS AND DISCUSSION

4.1. FTIR Test

As can be seen in Figure 1, FTIR spectra related to PU1 sample shows that clear absorption peak in 2270 that is related to the isocyanate group (-N = C = O) is not seen. In other hand there is the ability to see drawn bonds in the region 1635- 1770 (related to -C = O group of bond urethane) and also 3200-3500 area (related to -NH group of urethane bond). It is well clear that absorbed of carbonyl group of urethane bond that has hydrogen bond occurs compared to free groups at lower waves number, while the free carbonyl groups without hydrogen bond is clear in 1757-1753 area. Increase in the content of the hard part involves reduction in free carbonyl groups without hydrogen bond that is in FTIR

spectras related to the PU2, PU3 and PU4 samples in Figure2. The same situation also can be observed in polyurethanes which occurs the phase separation phenomenon it means that the two phases are separated from each other, one of the phases is to name of hard piece that had been include of diisocyanate and extender chain and another phase is to name of soft phase which is polyol amorphous. In order to change the properties of polyurethane, a simple solution is to change the ratio of hard piece to soft piece that can be done by changing the ratio of diisocyanate, polyol and extender chain during polymerization. For do a complete polymerization number of first monomers hydroxyl groups must be equal with first isocyanate groups numbers, too small amount of isocyanate causes the hydroxyl groups remain in system unreacted and sticky polymers with the lower molecular weight synthesize, while extra isocyanate lead to network formation of polymer and forming Allophonate connections. The ratio of initial isocyanate groups to the total of initial hydroxyl groups called isocyanate index.In some cases in order to improve the polyurethane molecular weight and its reaction progress, 1/05 excess amount of isocyanate is added to the mix. So The isocyanate index is greater than the 1/00 that the problem in this case is forming network and create Allophonate connections because excess amount of isocyanate which leads to gelation polymer and melt process the final polymer by conventional methods of melt forming such as extrusion and injection molding make faced with problem. Alophonat connections are reversible at high temperatures (that are not suitable for biodegradable polyurethane due to thermal degradation) and are re-formed with cooling. When the hard part will be increased in bond occurs the phase separation which can be attributed it to hydrogen bonding between data, with helping absorption spectrum of FTIR test calculated absorption intensity of synthesis samples and was calculated on the basis of equations

related to the phase separation degree and hydrogen bond index for samples ,which results are in Table (2). Presence of network connections in soft and hard part is caused creating spatial exclusion that prevent of hydrogen bond formation in soft part. In the polyurethanes as a result thermodynamically immiscible or incompatibility between the hard and the soft parts there are the possibility of phase separation. The phase separation degree depends to factors such as the type of diisocyanate, polyol, chain extender type and size of the soft and the hard part and increasing the hard part lead to degree increasing of phase separation.

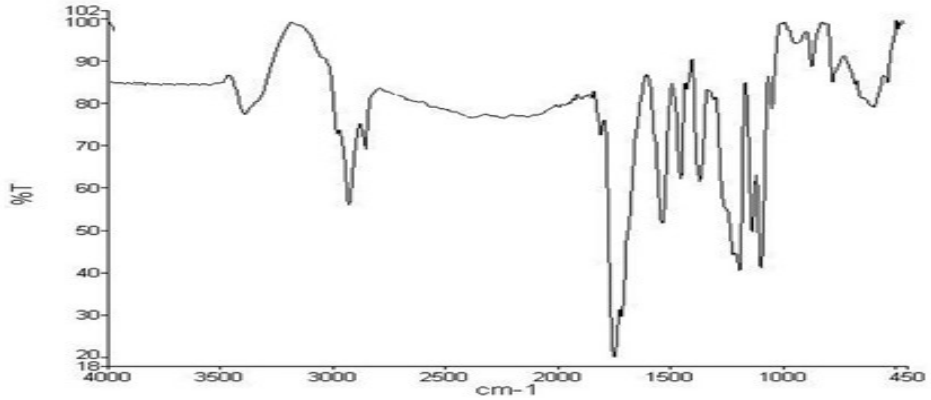

Figure 1: FTIR spectrum of PU1

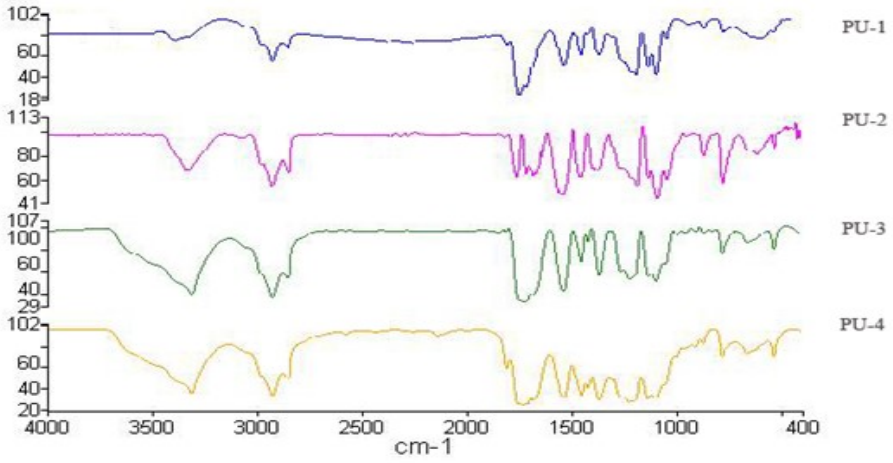

Figure 2: FTIR spectrum of PU1،PU2 ، PU3 و PU4 samples

Table 2: The degree of phase separation and hydrogen bond index polyurethane synthesized

sample	The phase separation	Hydrogen bond index
PU-1	0.33	0.23
PU-2	0.36	0.24
PU-3	0.38	0.25
PU-4	0.41	0.27

4.2. The results of TGA test

TGA the way of thermal weighing analysis is one of the most widely used method for evaluating the thermal stability in polymers. In this method the weight changes of synthesized polyurethanes samples were measured as a function of temperature. The method used was in this way that a small amount of polyurethane is placed in the device and device heated gradually and periodically to material. The amount of material that was placed in the device was only a few milligrams. The device recorded sample mass in its memory in different temperatures and finally data were plotted on a graph. The vertical axis represents the sample mass and the horizontal axis represents the temperature. Declining of graph showed this fact that with increasing temperature the sample mass is declining. Chart began from sample initial mass in the device. In the first the chart slope of all of synthesized polyurethane samples was stable and moved horizontally. This horizontal trajectory of chart was showed it that the polyurethane synthesized was pure and is not contain of impurities material and moisture, with increasing the temperature by other devices the graph was not again horizontal. This temperature was the material degradation temperature (Td) and from this temperature onwards the material was destroyed. Degradation temperature it is important thence that expresses with polyurethane synthesized to what temperature range can be worked and if the temperature is higher than the degradation temperature causes to the loss of sample. Polyurethane thermal stability depends to the chemical composition of materials that are used in its formulation. Based on obtained curves from the results of TGA test was

obtained destruction beginning temperatures of T_d and destruction %5 temperature of T0.05 and the remaining gray percentage obtained from polyurethane synthesized w (%). that this curves are in Figure (3), (4), (5) and (6) and related data of them are in Figure (3). As is clear in TGA curves we are witnessing the destruction of the two-stage from polyurethanes. The destruction of the first step is related to soft part (Poly Lactic acid-hidroxiled) and destroyed the second step is related to hard part (Hgzamtylndy diisocyanate, 1, 4 butane DL) synthesized polyurethane. Figure (3) curve related to pu-1 shows that the beginning temperature of the thermal degradation of polyurethane was 276° C and Figure (4) curve related to pu-2 shows the beginning temperature of the thermal degradation of polyurethane was 257° C and this temperature reduction is related to increasing the hard part and decreasing the soft part in synthesized polyurethane and in samples of pu-3 and pu-4 this drop is more that is in Table (3). With the increase of hard part in polyurethane decreased starting temperature of destruction and as can be seen in the above table this temperature with increasing of isocyanate and extender chain from 276 ° C arrived to 244 ° C. from all of above discussions in TGA test can be concluded that if hard part amount be greater in volume unit of polymer so termal stability of related polyurethane will be higher.

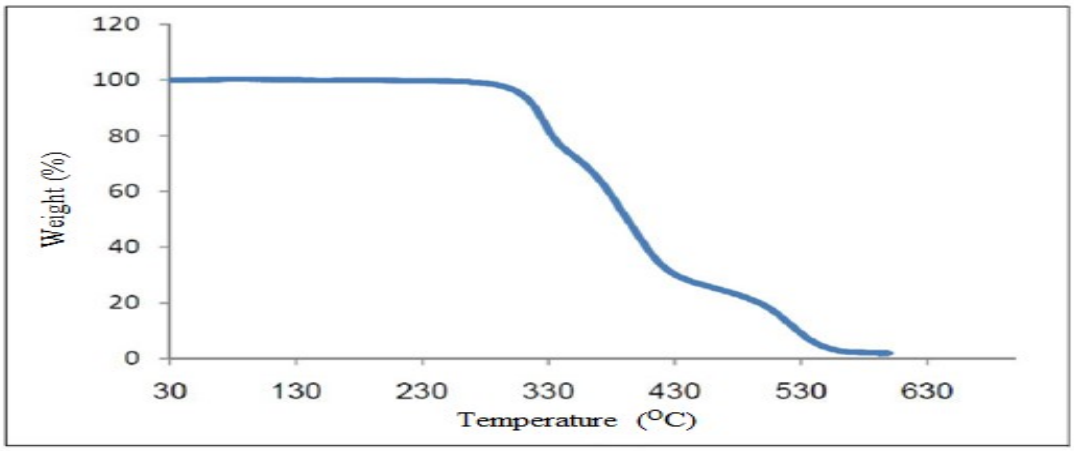

Figure 3: TGA curves of PU1 sample

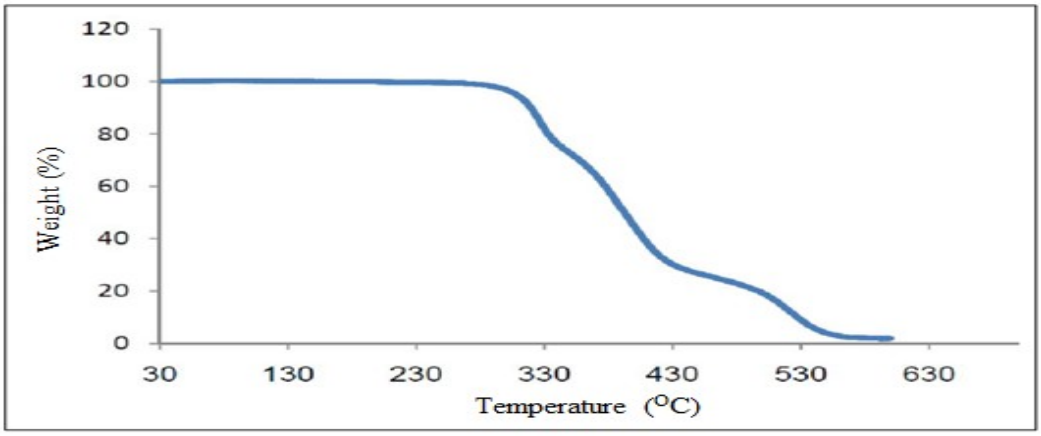

Figure 4: TGA curves of PU2 sample

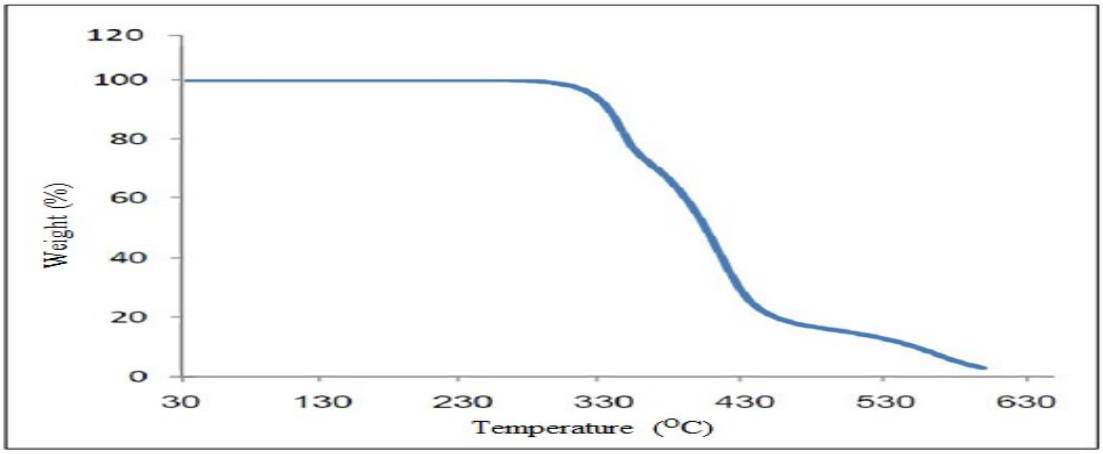

Figure 5: TGA curves of PU3 sample

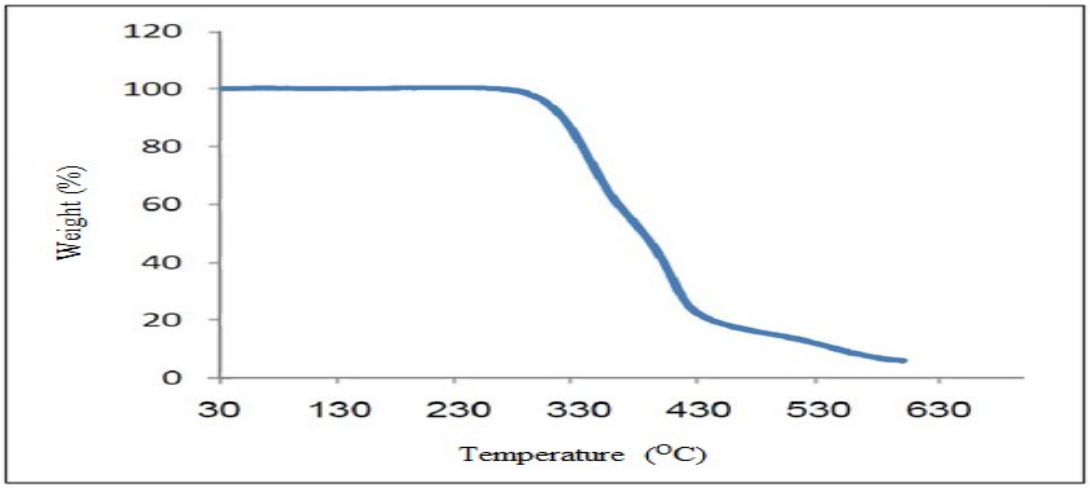

Figure 6: TGA curves of PU4 sample

Table 3: Comparison between TGA and DTG test data on the polyurethane Synthesized

sample	destruction beginning temperatures T_d (^oC)	destruction %5 temperature $T_{0.05}$ (^oC)	destruction of the first step T_{C1} (^oC)	destruction of the two step T_{C2} (^oC)	remaining persent w (%)
PU-1	267	323	392	464	1.7
PU-2	257	311	380	450	2.8
PU-3	249	308	375	445	3.2
PU-4	244	301	370	442	5.8

4.3. The results of DTG test

On the basis of obtained curves from results of DTG test obtained maximum temperature of synthetic polyurethane degradation (T_C) which this curves is in Figures (7), (8), (9) and (10) its related data are in Table (3). As we see on curves the related temperature to soft part is specified on the left side of curve and the related temperature of hard part is specified on the right side with curve drop.

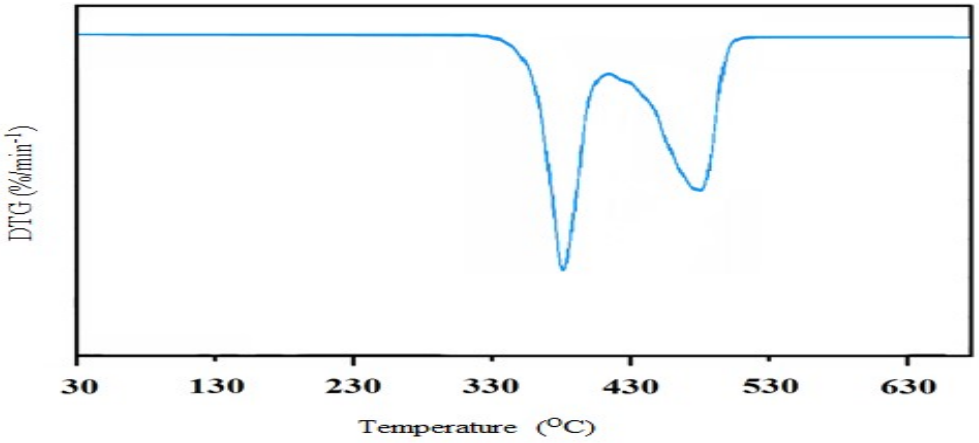

Figure 7. DTG curves of PU1 sample

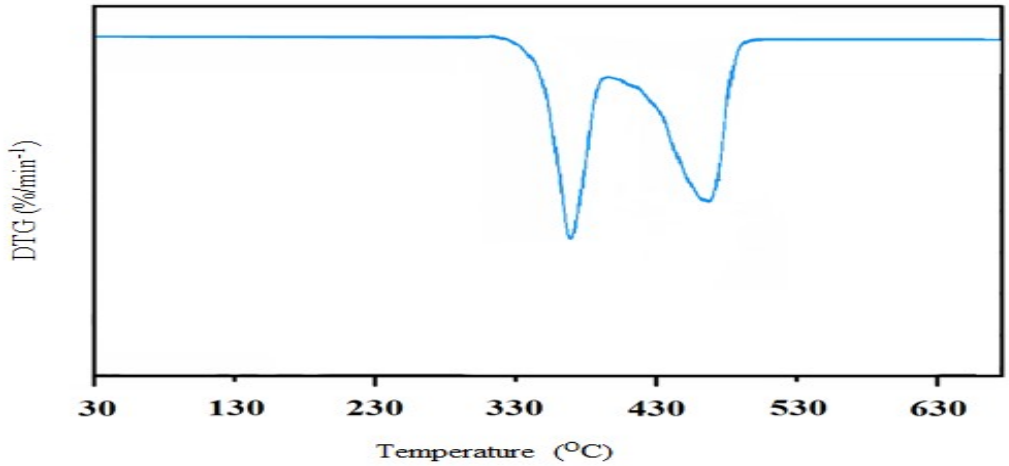

Figure 8. DTG curves of PU2 sample

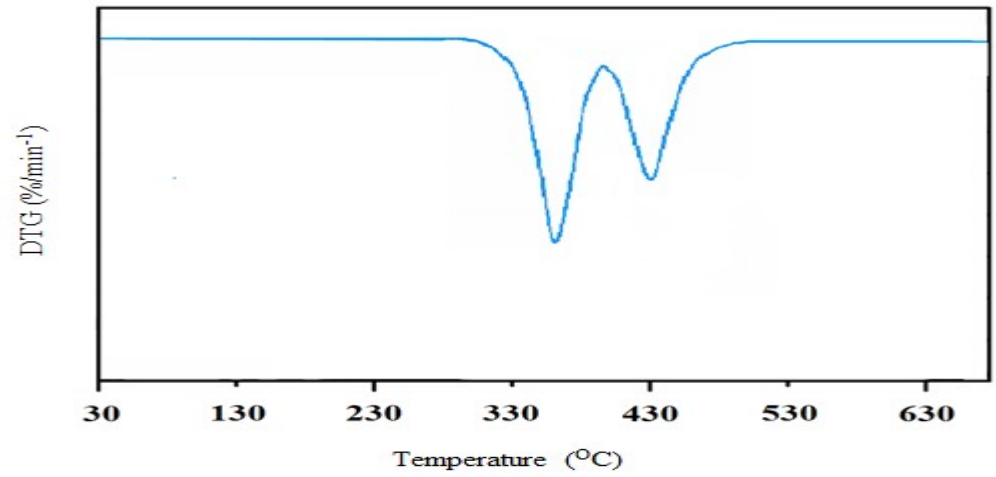

Figure 9. DTG curves of PU3 sample

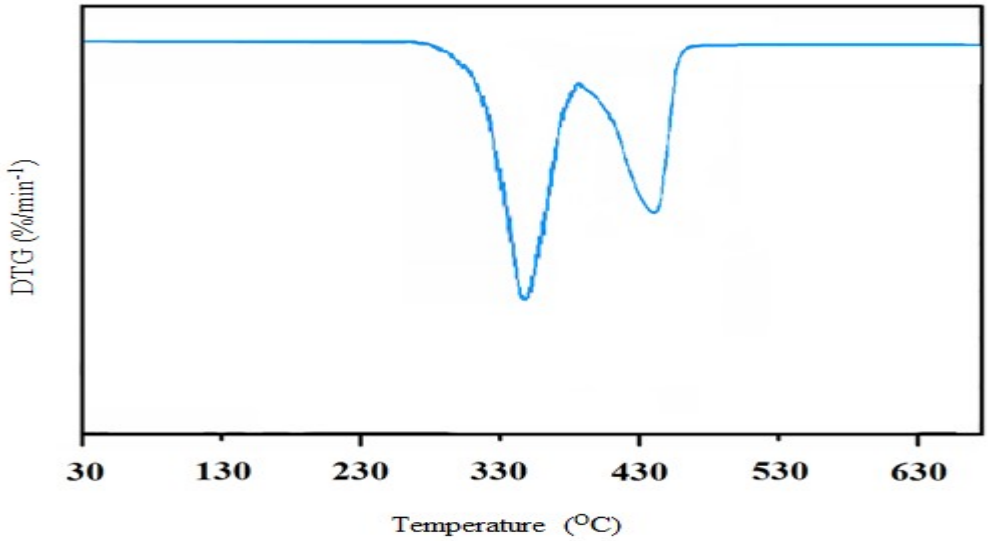

Figure 10.DTG curves of PU4 sample

4.4. The results of DSC test

Thermal analysis was performed by DSC test. This technique is a method of enthalpy change which in it difference of input energy to sample and reference were measured as a function of temperature degree. With DSC is widely used for polymeric testing for checking the melting point and sample glass transition temperature. The glass transition appears when the temperature of an object increases as a step in the beginning of the DSC. This step is the

result of it that with increase of temperature the object is getting a heat capacity change (doesn't phase change) and when the temperature rises finally the sample is melting. The result of melting process is an endothermic peak in the DSC curve. The melting temperature depends on the molecular weight, so for higher molecular weight is expected higher melting point. DSC curves related to samples of PU-1, PU-2, PU-3 and PU-4 are shown in order in Figures (11), (12), (13) and (14) and based on this test, the glass transition temperature and the melting temperature related to each of the synthesized samples was obtained that related data are in Table 4. In obtained curves first peak is related to Tg glass transition temperature and second peak is indicate of polyurethane Tm melting temperature. The content of the soft part (Poly Lactic acid-hidroxiled) is represent of glass properties in the low temperatures and reduce of this content transfers glass properties to lower temperatures. PU-1 sample that has more content of soft part than other samples in temperature of 47 ° C and PU-4 sample that has lower content of soft part than other samples in temperature 42 ° C going toward glass being. According to the obtained results can see that increasing of hard part amount (hex Mtylndy diisocyanate isocyanate and 1,4 butane DL) in synthesis of polyurethane leads to reduce of glass transition temperature and increase of melting temperature. From all discussions related to the results of TGA and DSC heat test can be concluded that if amount of the hard part increases in polyurethane volume unit the Intermolecular attractive force cross-linking in polymer chains causes strengthening physical properties and greater durability in higher temperatures and synthesized polyurethane was result of aliphatic diisocyanate that compared with the aromatic varieties have higher thermal stability. As a result thermal stability of related polyurethane will be more. The hard part depending on the amount of it in polyurethane is responsible of physical properties and

multiple melting points in higher temperatures. As in the recent few decades has been studied by many researchers, endothermic peak appeared at high temperatures can be because of the regular structures of the hard part, breaking the regular of chains long- range, or melting hard part in rich micro-phase of it. Increase the hard part in the synthesis of polyurethane, led to increase in molecular weight and increase the melting temperature and as that is clear PU-1 sample in temperature of 201 ° C and PU-4 samples in temperature of 211° C going to toward of melting.

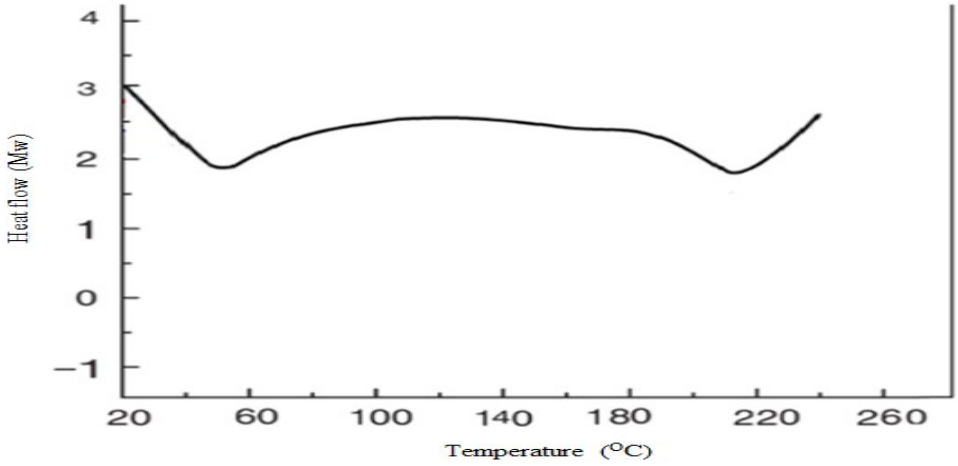

Figure 11: DSC curves of PU1 sample

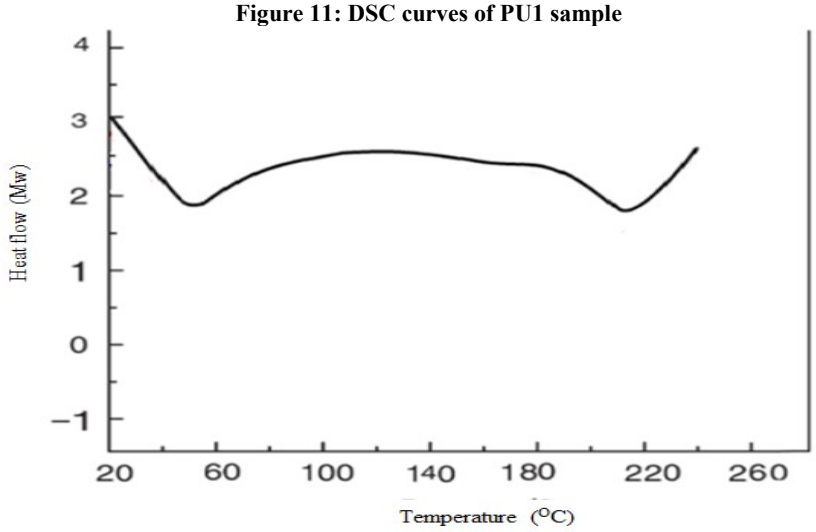

Figure 12: DSC curves of PU2 sample

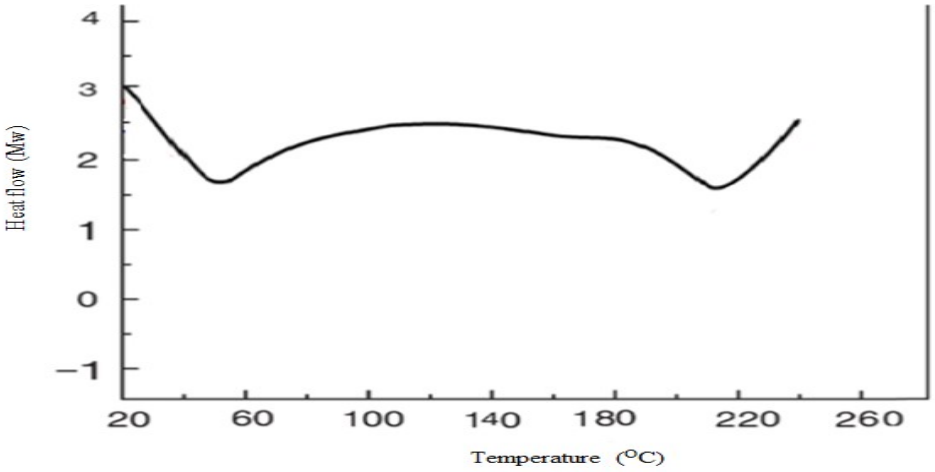

Figure 13. DSC curves of PU3 sample

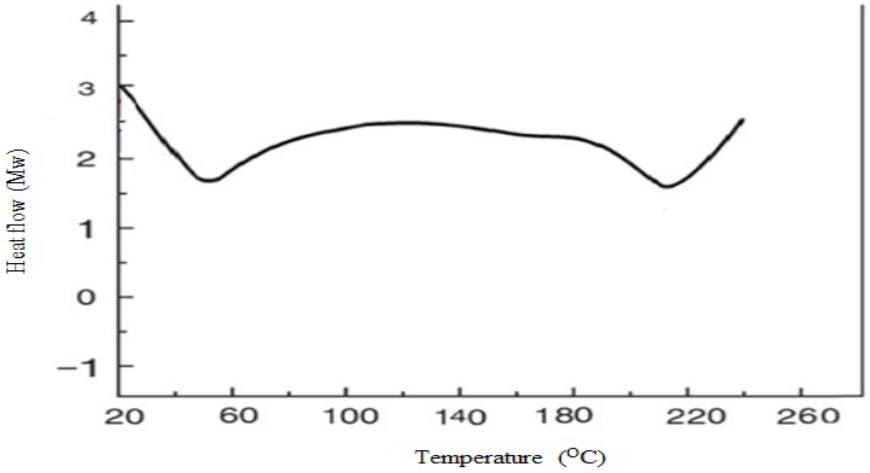

Figure 14: DSC curves of PU4 sample

Table 4: Results of DSC test polyurethane synthesized

Sample	Glass transition temperature Tg(°C)	melting temperature Tm (°C)
PU-1	**47**	**201**
PU-2	**45**	**204**
PU-3	**44**	**207**
PU-4	**42**	**211**

4.5. The results of GPS test

By gel permeation chromatography tests were calculated molecular mass of final polyurethanes. Numerical average molecular mass of $_n$ and the weighted average molecular mass of $_w$ was obtained and polyurethane with higher molecular weight was obtained that was our request. In the second step synthesis the resulting

pre-polymer chains were attached to each other by diisocyanate till poly (ester urethane) be prepared with higher molecular mass. Effect of molar ratio parameter of raw material (pre-polymer lactic acid and diisocyanate) and additional amount and the type of used isocyanate were investigated on molecular mass of final polyurethane. A huge increase in reaction time leads to produce the network polymer and insoluble in solvents. Therefore the best case for reaction time, according to the desirable results of this test is duration 6 hours for HDI isocyanates. As in Table (4) we are witness of this test results, particle distribution index declined with increases of hard part (% HS).

Table 4: Results of GPS test

Sample	% HS	$_n$ (GPC) ($*10^4$)	$_w$(GPC) ($*10^4$)	PDI
PU1	**18**	**3.6**	**5.8**	**1.61**
PU2	**25**	**4.4**	**6.6**	**1.50**
PU3	**32**	**5.1**	**7.3**	**1.43**
PU4	**39**	**5.5**	**7.8**	**1.42**

5. CONCLUSIONS

1. The resulting polyurethane was detected by FT-IR techniques, the results was indicate a successful synthesis of the product at each stage. When the hard part will be increased in bond the phase separation occurs which can be attributed to hydrogen bonding between data, absorption intensity of synthesized samples calculated with help of absorption spectrum of FTIR test and calculated on the basis of related equations to degree of phase separation and the hydrogen bond index for samples.

2. The results of the thermal analysis (TGA) and (DSC) were evaluated thermal stability of polyurethanes, by beginning temperature of decomposition and decomposition of constitutive products. In the synthesis of polyurethane the Increase of hard part amount (hexamethylene diisocyanate 1 and 4 butane DL) led to decrease in the glass transition temperature and increase of melting temperature.

3. Rheology test revealed high thermal resistance and desirable strength and The optimal properties of elasticity

polyurethanes and the results show that phase separation occurs usually in polyurethanes and is cause of tensile strength and high modulus of polyurethanes.

4- The results of this research is indicate of strong hydrogen bonds between the hard parts of obtained polyurethanes from aliphatic diisocyanates and increase of the hard part causes termal stability.

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