Analysis Mechanics and Thermal Composites Thermoplastic High Density Polyethylene with Zeolite Modification Filler

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Abstract

The purpose of the study to determine the thermal properties and mechanical properties of thermoplastic composites of high density polyethylene (HDPE) with filler natural zeolite modified with cetyl trimethyl ammonium bromide (CTAB) and purification of the calcination process.

Composite manufacture begins with a blens of calcined natural zeolites and zeolite synthesis CTAB. Then, the mixing of materials in an internal mixer at a temperature of 150^{o}C laboplastomil for 9 minutes. The results of the internal mixer and molded by hot press and cold press sheets that subsequently result in a dumbell with JIS K 6781 standard mechanical tests, ASTM D 3418-03 analysis thermal.

Mechanical analysis results showed values of tensile strength and elongation at break of HDPE with the highest composite filler modified zeolite CTAB/PE-g-MA at 24.964 MPa and 398.89 mm. The Young 's modulus of the highest indicated HDPE composites with zeolite filler CTAB was 720.76 MPa. While the results of the thermal analysis shows the value of the highest melting point and decomposition on HDPE composites with zeolite calcined/PE-g-MA at 151.23^{0}C and 488.23^{0}C.

Keywords : Zeolite, HDPE, CTAB, Mechanic, Thermal

1. Introduction.

Natural materials in general has hydrophilic properties, the material is generally not compatible with most polymer materials, therefore, must be chemically modified to make the surface more hidrofobis, it is necessary for a material that is compatible with the polymer matrix, (Sinto Jacob et al., 2010). Preparation of polymer composites made by combining two different materials so as to improve the mechanical properties of the material (Barleany, et al., 2011). Generally, the HDPE thermal, mechanical and bioactivity properties can be improved by the addition of inorganic particles into the polymer matrix (Fouad, et al., 2010). The HDPE has excellent low temperature toughness, chemical resistance, good dielectric properties and relatively high softening temperatures but poor weatherability. To take advantage of the natures of filler, many attempts have been made to improve the properties of HDPE blend by utilization of various inorganic fillers, such as $CaCO_3$ (Zebarjad, et al. 2006), graphite (Changzhi, et al. 2008) and bentonite (Bukit, et al. 2013).

Composite materials are those that are formed by the combination of two or more materials to achieve properties that are superior to those of their constituents (Wang et al., 2003). Due to the combination of more than one material, the properties of composites are influenced by many factors such as filler characteristics, filler content, and interfacial adhesion (Liang, 2006; Osman, et al., 2004).

This can cause the behaviour of filled polymers to be more complex than their unfilled counterpart. One way to make synthetic polymers such as polyethylene can be degraded is to make it into a HDPE polymer composites with a polymer matrix and nature as a filler that works to improve the physical properties of materials and components to reduce costs, speed up the printing process and enhance the thermal conductivity of the polymer as well as to increase the density and strength of the polymer, increasing the modulus and hardness of polymers (Xanthos, 2005). One of the natural polymers used as filler is zeolite. Zeolite is a natural mineral rocks or chemically belonged to the mineral silica and alumina silicate expressed as hydrated, smooth shape, and is the result of secondary products are stable at surface conditions (Sutarti, 1994). Natural zeolite generally has a low crystallinity, pore size is not uniform, low catalytic activity, and contains a lot of impurities. Therefore, it needs to be activated and modified before it can be used (Handoko, 2001). Zeolites containing aluminum silicate compound which has a three- dimensional framework structure is formed by tetrahedral AlO_4^{5-} and SiO_4^{4-} filled cavity in which metal ions are usually alkaline earth metals (Na, K, Mg, Ca and Fe) and water molecules tend to move freely in space intermilar cavity structure.

The activation process is done by heating physically. Heating aims to evaporate the water trapped in the pores of the zeolite crystals so that the number of pores and the specific surface area increases. Activation of chemically can be done by using a solution of hydrochloric acid or sulfuric acid or certain salts which aims to clean the surface of the pores, removing nuisance compounds and rearrange the layout of atoms can be exchanged (Suyartono et al., 1991). However, the results obtained in the manufacture is not homogeneous due to the polarity difference between polymers and natural fibers, to improve the interaction between the filler to the polymer matrix has been done in several ways. One way to do is to add a link compounds thus improving the interface and adhesion properties of the filler with the polymer matrix (Machado, 2000).

Compatibilizer a specific compound that can be used to integrate incompatible polymers into stable mixture through intermolecular bonding (Mehta, et al., 2007), (Liu, et al., 2008). Maleic anhydrate grafted polyethylene (PE-g-MA) is a material that is commonly used as compatibilizer. Cetyl Trimethyl Ammonium Bromide (CTAB) is necessary so that the formation of a stable emulsion stabilizer called surface active agent which are organic compounds that are amphiphilic, meaning having two groups, which are hydrophobic and the other hydrophilic nature. Layered silicates in their pristine state are hydrophilic, most of the engineering polymers are hydrophobic (Quan, et al, 2006). In recognition of these properties, it is then expected that addition of zeolite will significantly improve the mechanical and thermal properties of the HDPE/zeolite CTAB blend. In this research, a modified natural zeolites with two process. The first process of purification with HCl solution and calcination at a temperature of 600^{o}C for 2 hours and the second by using a surfactant Cetyl Trimethyl Ammonium Bromide (CTAB), these two materials are used as filler in HDPE thermopastic, which are mixed in an internal mixer at a temperature of 150^{0}C for 9 minutes. The resulting samples were analyzed thermal and mechanical properties.

2. Experimental

2.1 Matrials and Methods

Materials used in the study of natural zeolite, Copolimer HDPE Production of PT Titan Petrokimia Nusantara Indonesia, melting temperature of 136°C, density 0.941 g /cm3, filter paper, PE-g-MA production sigma aldrich USA, Cetyl Trimethyl Ammonium Bromide (CTAB) Merck Germany, $AgNO_3$, distilled water, Aquabides.

2.2 Instrumentation

Internal Mixer Laboplastomil Model 30 R150, Hydraulic Hot Press, Cold Press of 37 ton from Genno Japan, Universal Testing Mechanic, for simultaneous thermal analysis (DTA-TGA) Setaram TAG24., DSC Mettler Toledo type 821.

2.3 The Processing of Zeolite

Zeolites are still in the form of chunks of destroyed first, then crushed using a ball mill. The zeolite is crushed sieved using a 200 mesh sieve 0.2 mol (approximately 21.88 g of Cetyl Trimethyl Ammonium Bromide-CTAB) is dissolved into 300 ml of water and then heated to 80^{0}C temperature for 1 hour stirring a solution of zeolite A further 50 g 1000 ml of water is added and heated and stirred at temperature of 100^{o}C for 2 hours as a solution after heating and stirring, solution A and solution B are mixed. The mixture is added with distilled water to a volume of 1500 ml. then heated to 100^{o}C temperature for 1 h the mixture is filtered with a vacuum filter 2 g $AgNO_3$ is added with 100 ml of distilled water using a glass beaker. The purpose of the addition of $AgNO_3$ solution to eliminate bromide. The mixture is filtered using filter paper until it changes color to dark when using $AgNO_3$. If it still turns back mixed with distilled water and filtered again. Subsequently the mixture was dried in a microwave at a temperature of 100^{0}C for 1 day.

Preparation of zeolite calcined was carried out following the method described (Bukit, 2012). Briefly, zeolite was prepared by grinding the chunks of natural zeolite to obtain the powder with the size of 200 mesh, and the powder was divided. was purified using 2 M HCl solution with the ratio of zeolite (mass) to HCl solution (mL) of 1:10, by stirring the mixture using magnetic stirrer for 2 hours. Then, the mixture was calcined in a furnace at 600°C for 2 hours. In this study, both calcined zeolites and zeolite CTAB were used as filler and reinforcing agent.

2.4 Blends of HDPE-Zeolite Calcined and Modification CTAB Composite.

HDPE-zeolite composites were prepared by mixing HDPE, zeolite calcined, CTAB and PE-g-MA, with the composition as presented in Table 1. The mixture was placed in the internal mixer labo plastomill, and mixed at a temperature of 150°C, which is the melting point of HDPE, at a rate of 50 rpm for 9 minutes.

Table 1. Composition Blends

Material	The Quantity (wt%)				
HDPE	100	95	90	95	90
Zeolite Calcined	-	5	5	-	-
Zeolite Modification CTAB	-	-	-	5	5
PE-g-MA	-	-	5	-	5

2.5 Mechanical Properties Measurement

Tensile strength measurement was performed according to JIS K 6781 standard using Universal Testing Machine, at crosshead speed of 50 mm min^{-1}. Young's modulus (E), ultimate tensile strength (σ_{max}), and elongation at break (ε_b) were determined from the stress-strain curves

2.6 Thermal Analysis

Thermal analysis was performed with a Mettler Toledo DSC 821 type, following the method described in ASTM D 3418-03, by weighing about 10-12 mg sample into 40 mL crucible. The analysis was carried out using nitrogen gas at a flow rate of 50 ml/min, with temperature program of heating-cooling-heating with the temperatures of -30 °C to 160 °C, -75 °C to 270 °C. The temperature ramp of -15°C /min was applied for cooling process, and 15 °C /min for heating process.

Simultaneous thermal analysis (STA) was performed on TGA-DTA Setaram TAG 24, by scanning the sample over the temperature range of 50-600°C using nitrogen gas with the flow rate of 50 mL/min and a heating rate of 20 °C/min.

3. Result and Discussion

3.1 Mechanical characteristics.

In this study, mechanical properties of the samples include tensile strength, elongation at break, and Young's modulus, are measured in order to evaluate the effect to compare the performance of calcined zeolite and zeolite modification CTAB in Table 2. On Figure 1 shows the tensile strengths of the samples filled with zeolite.

Table 2. Properties Mechanicals Composite HDPE with Filler Zeolite Modification

	Tensile Strength (MPa)	**Elongation at Break (mm)**	**Young's Modulus (MPa)**
HDPE	23.543	221.25	709.95
HDPE / Zeolite Calcined	23.829	286.66	643.43
HDPE / Zeolite Calcined/ PE-g-MA	22.137	371.72	659.58
HDPE / Zeolite Modification CTAB	23.550	356.88	720.76
HDPE / Zeolite Modification CTAB / PE-g-MA	24.964	398.89	679.81

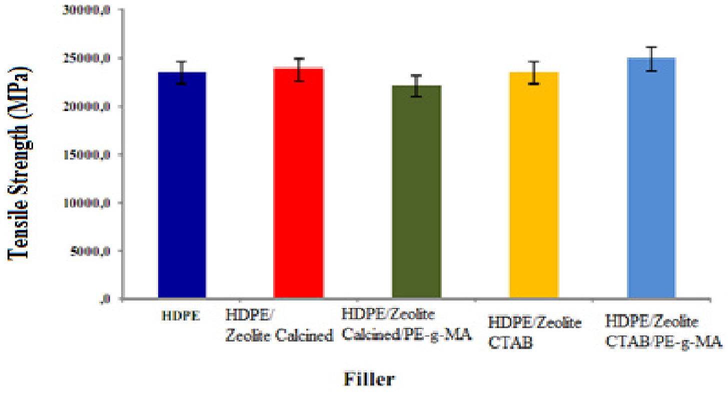

Figure 1. Tensile Strength of The Samples Filled

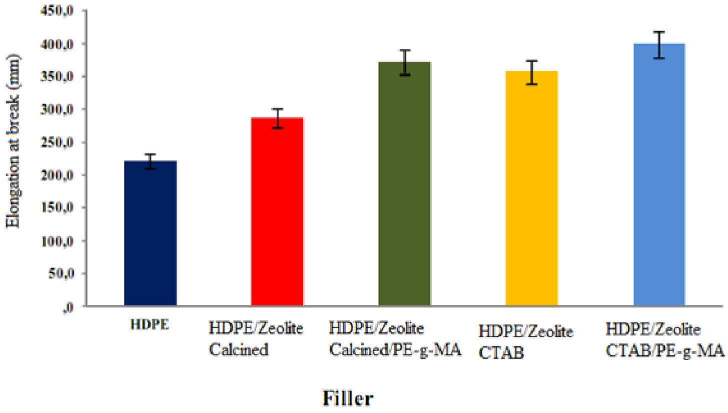

Figure 2. Elongation at break of The Samples Filled

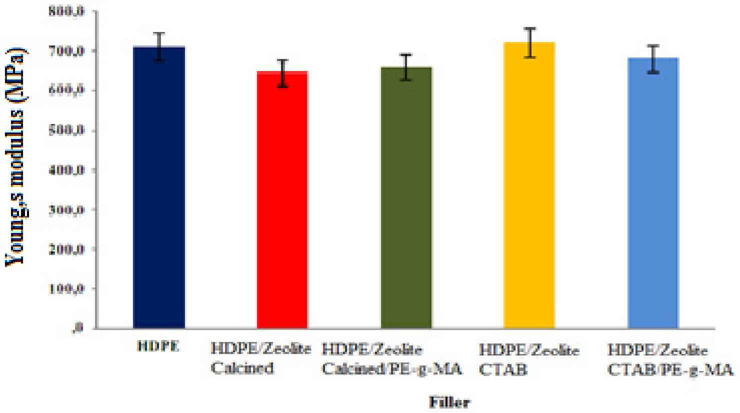

Figure 3. Young’s Modulus of The Samples Filled

From Table 2 obtained a large general increase in tensile strength with filler blends of HDPE natural zeolite synthesis CTAB/PE-g-MA is where the value of 24.964 MPa tensile strength, and increased of the value of 1.421 MPa tensile strength of HDPE thermoplastic natural zeolite particles carried by calcination process it can show in Figure 1. The increasing in tensile strength is probably due to the natural zeolite silicate layers dispersed randomly and evenly exfoliate that gives structure to the composite. Silicate layers that exist in zeolites are widely dispersed individually have a large contact surface so that it can bind strongly to the matrix HDPE and compatibelizer PE-g-MA which further give effect to the increase in tensile strength. The incorporation of the natural zeolite without PE-g-MA on the contrary a negative effect which lowers the tensile strength. This is probably due to the decrease in the degree of spread of exfoliation of silicate layers in the composite of natural zeolite addition, the agglomerate natural zeolite particles causes a decrease in tensile strength. Agglomeration natural zeolite is believed to be a stress concentration point and the beginning of the crack so that the power will go down. Figure 2 shows that HDPE composites with filler natural zeolite synthesis CTAB/PE-g-MA has the highest value of elongation at break of 398.89 mm, and an increase of 177.64 mm from the value of elongation at break of HDPE thermoplastic. Figure 3 shows the Young's modulus of the HDPE composite filler calcined zeolite and zeolite modified CTAB, where the filler zeolite modification with CTAB has a greater value than the zeolite.

In general, mechanical properties (tensile strength, elongation at break, and Young’s modulus) HDPE composites with filler natural zeolite synthesis CTAB resulted in the value -added mechanical properties include tensile strength , elongation at break , and Young,s modulus. This is due to the nature of the CTAB surfactant on the synthesis of natural zeolite particles resulting CTAB particles formed easily dispersed, so that the mixture is more homogeneous composites. The particle size of the filler material can increase the reinforcement of polymers small compared with the large particle size (Leblance, 2002). Particle size has a direct relationship to the surface area per gram of filler material. Small particle size provides a large surface area for interaction between the polymer matrix and filler so improve reinforcement of polymeric materials. The smaller the particle size the higher the interaction between filler and polymer matrix. This is consistent with the results of the study (Kohls et al., 2002) states that the surface area can be increased by the presence of surface air at the surface of the pore filler. It is possible that the polymer can penetrate into the pore surface when air mixing process. Particles dispersed homogeneously enhancing interactions through polymer adsorption on the surface of the filler. Conversely particles homogeneously dispersed may produce clots in the polymer matrix. Existence of agglomerates subtracting the surface area so weaken the interaction between filler and matrix and lead to a decrease in the physical properties of polymeric materials.

3.2 Thermal Properties.

In this study, thermal characteristics of the samples were evaluated by analyzing the samples with differential thermal analysis (DTA), thermal gravimetric analysis (TGA) and Differential scaning calorimetry DSC. Thermal properties of the data can be seen in Table 3.

Table 3. Analysis Thermal Composite HDPE with Filler Zeolite Modification

Sample	On Set Temperature (^{o}C)	Top of Temperature peak(^{o}C)	Tg (mg)	Enthalpy (micro V.s/mg)	Decomposition (^{o}C)	Tg (mg)	Enthalpy (micro V.s/mg)
HDPE	124.27	140.13	0.64	-43.411	448.47-475.70	-26.21	-60.998
HDPE/Zeolite Calcined	131.23	146.80	-0.04	-42.173	458.93-485.17	-21.29	-87.079
HDPE/Zeolite Calcined/PE-g-MA	133.47	151.23	-0.13	-57.367	461.10-488.23	-25.37	-151.947
HDPE/Zeolite CTAB	134.93	147.53	-0.11	-25.572	464.50-483.53	-27.07	-146.488
HDPE/Zeolite CTAB/PE-g-MA	124.27	138.63	-0.01	-18.327	442.93-484.57	-19.10	-91.445

Figure 5 and 6 can be seen an increase in the melting point with the addition of fillers of calcined natural zeolite and calcined zeolite with kompatibiliser PE-g-MA because it has high thermal properties so that when combined with HDPE can increase the melting temperature of the mixture as well as an increase in the decomposition temperature. Thermal analysis of the data in Figure 4 HDPE thermoplastic pure melting point range (124.7-140.13)^{0}C, when compared with HDPE composite zeolite modification with CTAB, zeolite calcination has a melting point greater decomposition temperature as well as can be seen in Figure 7 and 8, but in general, the melting point and decomposition temperature greater than the melting point of pure HDPE. Figures 8 and 9 show the results of thermal analysis by DSC in which the melting point of the filler calcined zeolite compatibilizer with PE-g-MA is larger than the zeolite CTAB Improved thermal stability of mixtures of HDPE/calcined Zeolite/PE-g-MA is a strong interfacial adhesion between the filler natural zeolite with matrik HDPE that arise from the addition of functional groups malead anhydride (Joseph, et al, 2003), (Bukit, et al, 2013), where the group maleated anhydride functionalization on PE-g-MA increases the bonding between the filler with the matrix face. The Variable considered polymer heat stable or heat resistance, the polymer must not decompose temperatures below 400^{0}C and must maintain its useful at temperatures close to the decomposition. The compatibelizer addition of PE-g-MA can be improved the degree cristality HDPE composites containing calcined zeolites and zeolite CTAB, this is caused by the chain branching between maleic anhydride and better dispersion between PE-g-MA in the polymer material (Pracell, et al., 2006). Higher crystallinity of calcined zeolite promoted thermal stability of the composite, leading to higher decomposition temperature.

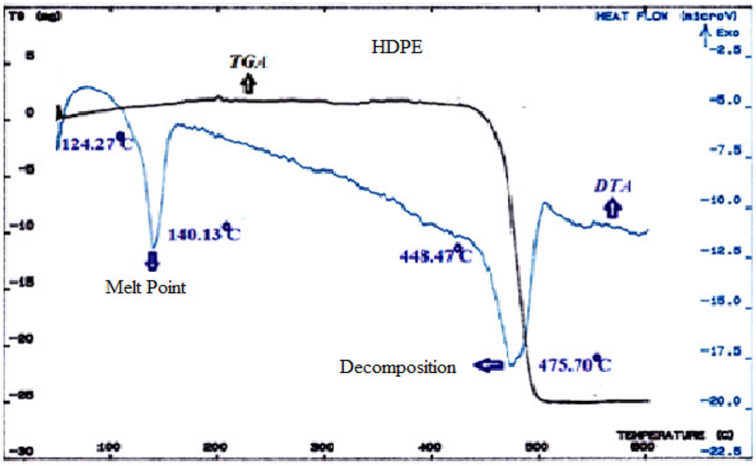

Figure 4. TGA-DTA Thermogram of The Samples Filled HDPE

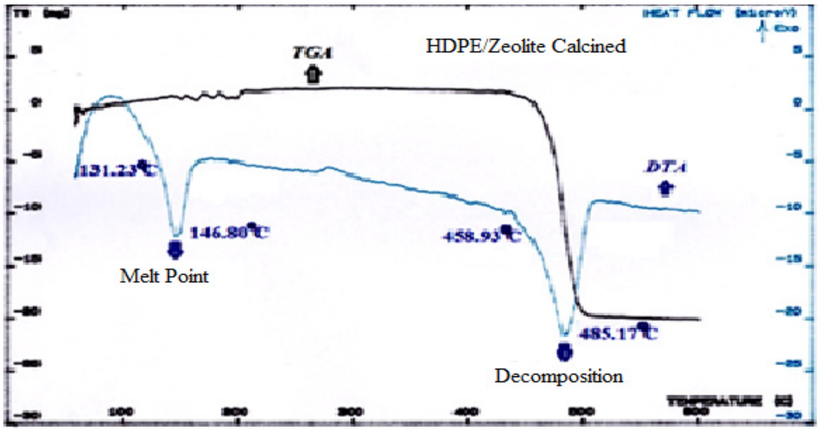

Figure 5. TGA-DTA Thermogram of The Samples Filled HDPE/Zeolite Calcined

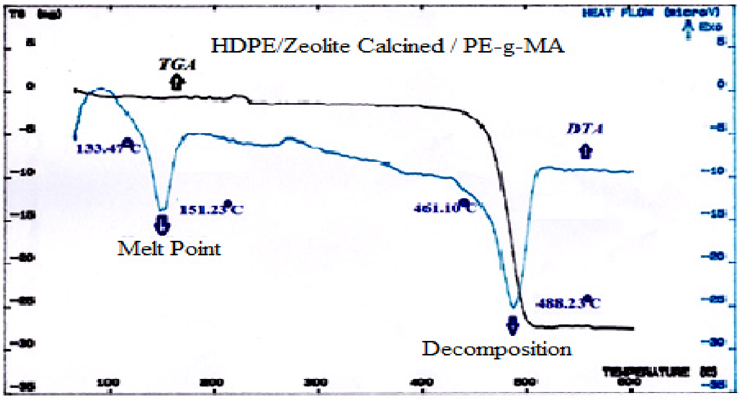

Figure 6. TGA-DTA Thermogram of The Samples Filled HDPE/Zeolite Calcined /PE-g-MA

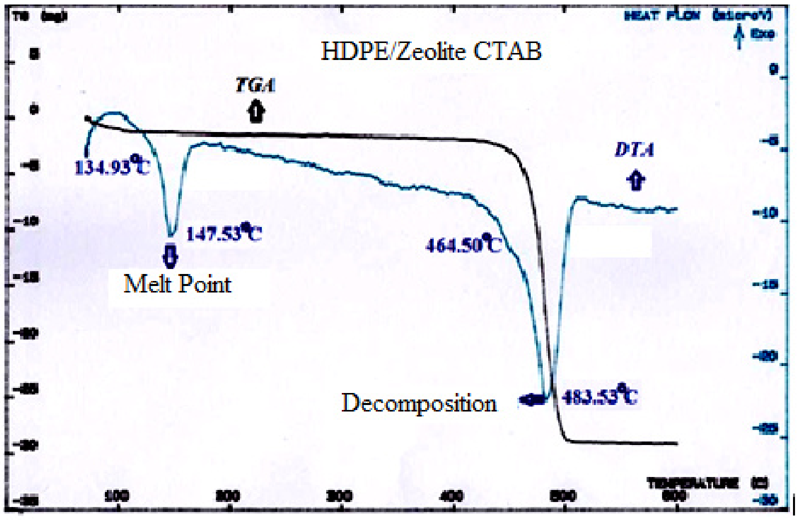

Figure 7. TGA-DTA Thermogram of The Samples Filled HDPE/Zeolite CTAB

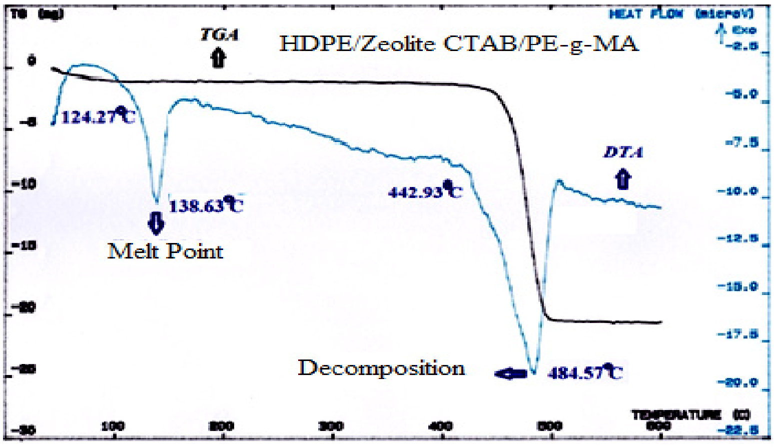

Figure 7. TGA-DTA Thermogram of The Samples Filled HDPE/Zeolite CTAB/PE-g-MA

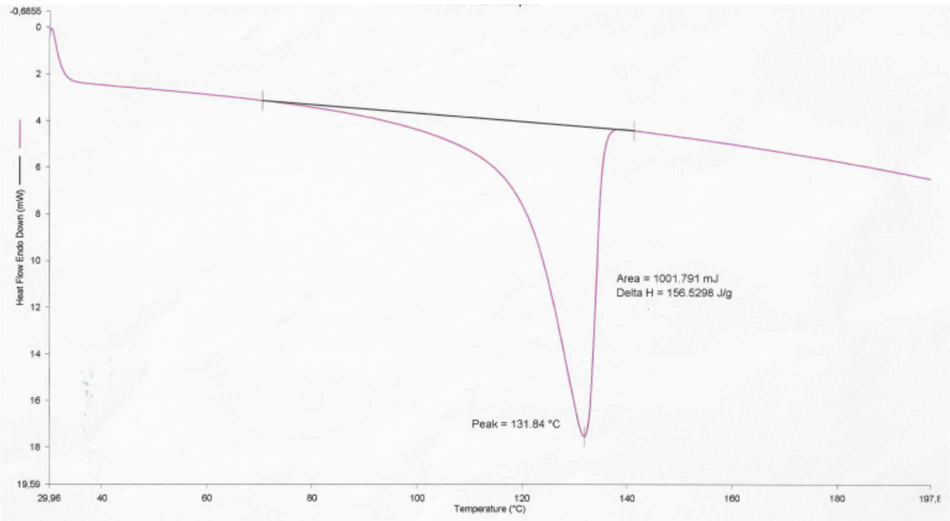

Figure 8. DSC Thermogram of The Samples Filled HDPE/Zeolite Calcined /PE-g-MA

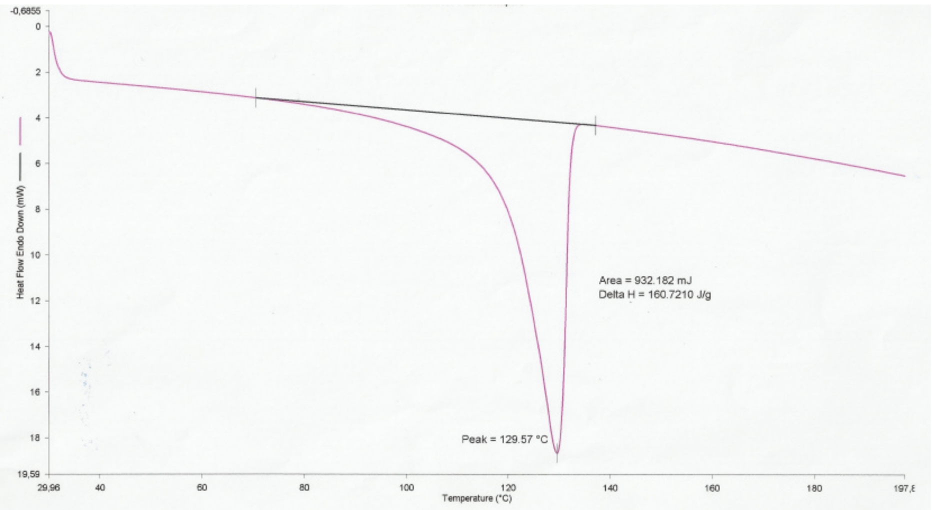

Figure 9. DSC Thermogram of The Samples Filled HDPE/Zeolite CTAB/PE-g-MA

4. Concolusions

Results of analysis of mechanical (tensile strength and elongation at break) was highest in the composite HDPE with fillers zeolite CTAB/PE-g-MA at 24.964 MPa and 398.89 mm, Young's modulus is the highest found in the composite HDPE with fillers zeolite CTAB was 720.76 MPa.

Thermal analysis results obtained by melting and decomposition of the biggest in the HDPE composites with filler calcined zeolite/PE-g-MA, the melting point 151.23^{0}C and decomposition of 488.23^{0}C. Crystallinity of calcined zeolite promoted thermal stability of the composite, leading to higher decomposition temperature.

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