MECHANICAL AND THERMAL PROPERTIES OF POLYPROPYLENE REINFORCED BY CALCINED AND UNCALCINED ZEOLITE

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Abstract

This study was carried out to compare mechanical and thermal properties of polypropylene (PP) reinforced with uncalcined and calcined zeolites. The PP samples were reinforced with zeolites at various quantities of 2, 4, and 6 (wt %). The comparison of the two types of zeolite was based on mechanical properties, including tensile strength, elongation at break, and Young's modulus, and thermal characteristics analyzed using DSC, and DTA/TGA technique. The results obtained clearly revealed that both zeolites were able to significantly increase tensile strength and Young's modulus of the samples, with calcined zeolite was found to work better. Addition of calcined zeolite was found to result in increased fracture elongation of the samples reinforced with up to 4 wt% zeolite but decreased sharply for the sample reinforced with 6 wt% zeolite, while for the samples reinforced with uncalcined zeolite, no consistent trend was observed. Thermal analyses demonstrated that the samples reinforced with calcined zeolite are more resistant to thermal treatment than those reinforced with uncalcined zeolite, as indicated by their higher decomposition temperature. DSC analysis revealed that there was no significant difference of the melting points of the samples was observed, but the effect of the quantity of zeolite on enthalphy was quite evident, in which the enthalpies of the samples reinforced with calcined zeolites were relatively lower than those of the samples reinforced with uncalcined zeolites.

Abstrak

Sifat Mekanik dan Termal dari Polipropilena Diperkuat dengan Zeolit Tanpa Kalsinasi dan Zeolit Kalsinasi.
Penelitian ini bertujuan untuk membandingkan zeolite tanpa kalsinasi dan yang dikalsinasi sebagai penguat polipropilena (PP). Sampel PP diperkuat dengan zeolite dengan jumlah yang berbeda, yakni 2, 4, dan 6% berat. Sifat mekanik yang diamati adalah kekuatan tarik, perpanjangan putus dan modulus Young. Sifat termal dianalisis dengan menggunakan DSC dan DTA/TGA. Dari hasil penelitian ini diperoleh kekuatan tarik dan modulus Young zeolit kalsinasi meningkat. Perpanjangan putus pada penambahan zeolit sampai 4% mengalami peningkatan namun terjadi penurunan pada penambahan 6%. Zeolit tanpa kalsinasi menunjukan perpanjangan putus lebih rendah dari zeolit kalsinasi. Analisis termal dengan DTA/TGA pada zeolit kalsinasi memiliki daya tahan termal lebih tinggi dibandingkan dengan zeolit tanpa kalsinasi, yang ditandai dengan peningkatan temperatur dekomposisi zeolit kalsinasi. Dari analisis DSC didapatkan bahwa tidak ada perbedaan yang sigifikan antara titik lebur sampel, namun sampel yang diberi zeolite kalsinasi memiliki entalpi yang relatif lebih rendah.

Keywords: PP, PP-g-MA, zeolite, analysis, mechanical, thermal

1. Introduction

Polypropylene (PP) is a thermoplastic polymer used in a wide variety of applications. PP is one of the most important commercial polymers due to its superior properties such as high melting temperature, high chemical resistance and low density. However, this polymer is characterized by low elastic modulus, poor physiochemical properties, low thermal resistance as well as mechanical properties, which necessitate reinforcement in order to meet required properties. To overcome these limitations, PP is commonly used in combination with other materials such as fillers or reinforcing agents to enhance its properties and increase its suitability for specific applications. Addition of filler is aimed not only to fill the PP matrix with small particles, but also to modify the matrix texture as a result of interaction between the PP molecules with the particles of reinforcing agent during processing. By addition of proper filler, it is then possible to produce

modified PP with improved properties, such as thermal and mechanical properties. As an example, high specific surface area of the fillers is expected to enhance interphase effects and tensile strength of the PP [1]. For this purpose, different types of reinforcing agents have been used, such as $CaCO_3$ [2], talc [3], mica [4], and glass fiber [5].

Another potential material as reinfrocing agent for polymers is zeolite. Natural zeolite is microporous crystalline, hydrated alumina silicates of alkaline and alkaline earth element with regular pore structures and high thermal stability [6-7], which imply that addition of zeolite will improve thermal properties of the polymers. In addition, this mineral is resistant to organic solvents, chemicals, and it has high tensile strength and elasticity, as well as hardness which make it resistant to mechanical stress. Furthermore, natural zeolites are abundant and they are considered as low-cost materials. In Indonesia, natural zeolites are available in abundance and can be found in various regions in Java, Sulawesi, and Sumatra. One of the main locations of natural zeolite in Sumatera is Pahae, situated in District of North Tapanuli, the Province of North Sumatera.

There are many studies dealing with the use of zeolite as reinforcing agent for polymer, in which both uncalcined and calcined zeolites have been tested [8-9]. In previous study [10], it was reported that reinforcement of PP with zeolites led to significant improvement in the mechanical properties, and the samples reinfroced with calcined zeolites exhibit better properties. This difference effects is presumed as a result of better interfacial interactions of calcined zeolite than that of uncalcined zeolite. Pehlivan, *et al.* [11] also confirmed that PP reinforced with calcined zeolite has higher mechanical and thermal stability compared to the PP reinfroced with uncalcined zeolite. The main reason which makes calcined zeolite works better is most likely higher density and smaller pores compared to the uncalcined zeolite, leading to stronger interfacial interaction between calcined zeolite and PP matrix.

Apart from its good characteristics as reinfrocing agent, hydrophilic nature of zeolite makes this material less compatible with most organic polymers. One method to overcome this drawbacks is by addition of compatibilizer, which functions to reduce the hydrophobicity of the polymer by creating hydrophilic moeities on the surface. For this purpose, several compatibilizers have been investigated, such as graphene oxide [12], graphene/polymer [13], graphene/ polyacrylamide [14], and PP-g-MA [15]. In this study, the compatibilizer used was PP-g-MA since this compatibilizer is structurally more suitable with the PP.

The general objective of this study is to compare the efficacy of uncalcined and calcined zeolite as reinfrocing agents on mechanical and thermal properties of PP, with specific goal to investigate the effects of the quantity of zeolites loaded.

2. Methods

Materials. Polypropylene (PP) was obtained from Production Singapore. This polymer has melting point of 178 °C, and density of 0.896 g/cm^3. Polypropylene grafted maleic anhydride (PP-g-MA) was obtained from Japan. Natural zeolite was obtained from Pahae, District of North Tapanuli, the Province of North Sumatera.

Instrumentation. The instruments used are Haake Internal Mixer Rheocord 90 (Labo Plastomill Model 30 R150 chamber volume 60 cc), Hydraulic Hot press, cold press of 37 ton from Gennō Japan. Ball mill, HEM-E3D, Planetary Ball mil PBM-4, Universal Testing Mechanics model Laryee Machine Universal Testing Wdw-10, Furnace, Particle Size Analyzer Desla^{TM} nano, DSC Mettler Toledo type 821, for Simultaneous thermal analysis STA (TGA-DTA) Setaram TAG24.

Preparation of zeolites. In this study, both uncalcined and calcined zeolites were used as reinfrocing agent. Preparation of zeolite was carried out following the method described by Bukit [16]. 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 into two parts. The first part was grinded for 10 hours using planetary ball mill PBM 4. After this treatment, the zeolite was found to have the particle size of 144.8 nm, and specified as uncalcined zeolite. The second part 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, before the sample was grinded using planetary ball mill PBM 4 for 10 hours. This sample is specified as calcined zeolite, and has the particle size of 190.2 nm.

Preparation of PP-zeolite Composite. PP-zeolite composites were prepared by mixing PP, zeolite and PP-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 178 °C, which is the melting point of PP, at a rate of 60 rpm for 10 minutes.

Mechanical properties measurement. Tensile strength measurement was performed according to JIS K 6781 standard using a Laryee Universal Testing Machine Wdw-10, at crosshead speed of 50 mm min^{-1}. Young's modulus (E), ultimate tensile strength (σ_{max}), and fracture elongation (ε_b) were determined from the stress-strain curves.

Table 1. Composition of the PP-Zeolite Compsite Prepared

Sample	PP (wt%)	PP-g-MA (wt%)	Calcined zeolite (wt%)	Uncalcined zeolite (wt%)
S_0	100	0	0	0
S_1	95	5	0	0
S_2	93	5	2	0
S_3	91	5	4	0
S_4	89	5	6	0
S_5	93	5	0	2
S_6	91	5	0	4
S_7	89	5	0	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. Results and Discussion

Effects of zeolites on the tensile strength. In this study, mechanical properties of the samples measured are tensile strength, fracture elongation, and Young's modulus. Figure 1 represents the tensile strengths of the samples reinforced with both uncalcined and calcined zeolite at different quantities (wt %).

As seen in Figure 1, for the samples reinforced with uncalcined and calcined zeolites, the tensile strengths are higher than that without zeolite addition, demonstrating the significant role of zeolite as reinforcing agent which enhance the capability of the samples to assume tensile. For the samples reinforced with calcined zeolite, the highest strength was displayed by the sample reinforced with 2 wt% zeolite, and progressively decreased as the quantity of the zeolite was increased. This result appears to suggest that at small amount (2 wt%), zeolite molecules are distributed homogeneously in the matrix of the PP blend, producing strong interaction between zeolite and PP matrix, while at higher amounts agglomeration of zeolite molecules is likely to be more prominent, hindering the distribution of some of the molecules into the matrix of the PP blend [1]. For the samples reinforced with uncalcined zeolite,

the tensile strength of the samples due to addition of zeolite displays slightly different pattern to that observed for the samples reinforced with calcined zeolite, in which no evident difference of the tensile strengths was observed although there is a tendency that the highest value is displayed by the sample reinforced with 4 wt% zeolite, suggesting that interfacial wettability and adhesion between PP and zeolite was improved. Overall, the results indicated that the tensile strength of the sample reinforced with uncalcined zeolite is relatively lower than that of the sample reinforced with calcined zeolite at the same amount up to addition of zeolite of 4 wt%, but for addition of zeolite of 6 wt%, the opposite is true. This result suggests that the particles of uncalcined zeolite exhibit smaller ability to incorporate with the chain of PP molecules compared to those of the calcined zeolite, with the exception of the sample reinforced with 6 wt% zeolite, probably due to more prominent agglomeration of the particles of the calcined zeolite, as has been previously described [17-18]. Higher tensile strength of the sample reinforced with 6 wt% of uncalcined zeolite compared to that of the corresponding sample reinforced with calcined zeolite, is most likely related to the presence of more silanol (Si-OH) groups in the uncalcined zeolite, which capable to form strong bonding with the PP molecules [19].

The effect of zeolites on the fracture elongation. The fracture elongation of the samples reinforced with uncalcined and calcined zeolite are shown in Figure 2, indicating that uncalcined and calcined zeolite imparted quite different effects on the PP blend.
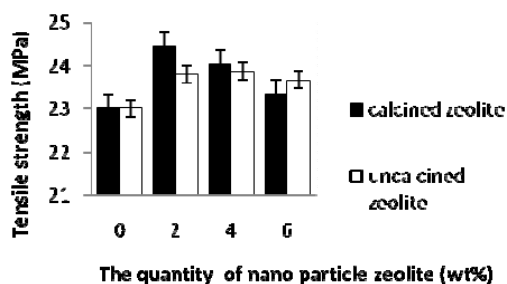

Figure 1.   Tensile Strength of the Samples Filler with Uncalcined and Calcined Zeolite
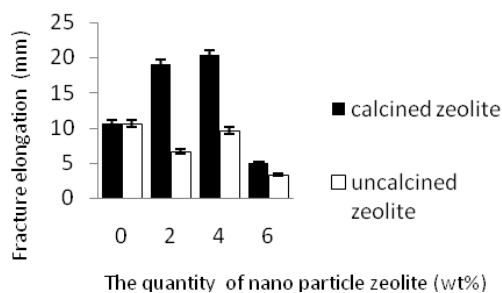

Figure 2. Fracture Elongation of the Samples Reinforced with Uncalcined and Calcined Zeolite

The fracture elongation of the samples filled with uncalcined zeolites is smaller than that of the sample without zeolite addition. This finding is in accordance with the properties of uncalcined zeolite as rigid and hydrophilic material due to the presence of silanol groups on the surface. As rigid material, addition of uncalcined zeolite will cause the PP-zeolite composite become more brittle than pure PP, and addition of more zeolite resulted in decreased fracture elongation as a consequence. In addition, the hydrophilic nature of uncalcined zeolite makes the molecules less compatible with the PP molecules, leading to poor incorporation between the molecules of the two materials.

The results observed from the samples reinforced with calcined zeolites are significantly different with those observed for the samples reinforced with uncalcined zeolites. The results clearly displayed that calcined zeolite functions more as plasticizer rather than reinforcing agent, except for the sample reinforced with 6 wt% zeolite. The action of calcined zeolite as plasticizer is most likely due to hydrophobic surface of the zeolite molecules, making the molecules very compatible with the PP molecules, leading to the enhancement of adhesion between zeolite and PP matrix to produce more flexible composite. Plasticizing effect of calcined zeolite observed in this study is in agreement with the results of other [20], who suggested that the plasticizing effect resulted from the formation of physisorbed layer in the interphase of the composite. During the blending process, the particles of zeolite were scattered randomly, producing larger surface contact area, which result in strong binding of the zeolite particles with the PP blend, increasing the ability of the sample to assume elongation. The exception for the sample reinforced with 6 wt% zeolite is most likely due to excessive number of molecules present, causing more prominent agglomeration of zeolite molecules during the blending process, resulted in deformability of the composite.

Apart from different trends observed, it could be seen that the fracture elongation for the sample reinforced with calcined zeolite is much higher, around two to fourfold, than that of the sample reinforced with uncalcined zeolite at the same amount. Smaller fracture elongation of the samples with uncalcined zeolite strongly suggest that incorporation of the particles of the uncalcined zeolite with the molecules of PP was more difficult due to more prominent agglomeration of the zeolite particles, therefore reduces the elasticity of the PP chains as a consequence.

The effect of zeolites on the Young's modulus. Figure 3 represents the Young's modulus of the samples reinforced with uncalcined and calcined zeolite, displaying that practically no significant difference between the samples, both in terms of the general trend and value of the modulus.

As shown in Figure 3, for the two set of samples, stepwise increase of the Young's modulus was observed with the addition of zeolite up to 4 wt% and decreased for the samples reinforced with 6 wt% zeolites. These results are in agreement with the results for tensile strengths, since Young's modulus is linearly proportional with tensile strength, while with fracture elongation the opposite is true. Addition of more zeolite will promote the capability of the composite to carry more tensile load as a result of increased tensile strength and decreased fracture elongation.

In general, the results obtained demonstrated that the samples reinforced with calcined zeolite display slightly higher Young's modulus than that of the sample reinforced with uncalcined zeolite at the same amount. This result implies that the samples reinforced with calcined zeolite are relatively more compact than that reinforced with uncalcined zeolite, probably due to more homogeneous distribution of the particles of the calcined zeolite in the PP matrix [21]. Decreased Young's modulus of the samples reinforced with 6 wt% zeolites reflects that filling of the PP with zeolite higher than 4 wt% might lead to decrease in the degree of spread of exfoliation of the silicate layers of zeolite in the PP matrix [10,18].

Thermal Analysis. In this study, thermal characteristics of the samples were evaluated by analyzing the samples with differential thermal analysis (DTA) and thermal gravimetric analysis (TGA). The TGA thermograms of the samples reinforced with different amounts of uncalcined zeolite are compiled in Figure 4, and the corresponding DTA results are presented in Figure 5.

The TGA results presented in Figure 4 indicate that up to temperature of 387 $^{\circ}$C, no weigh loss was practically observed, which means that up to this temperature, no decomposition of the samples took place. At temperature ranging from 378 to 497 °C, the results indicate very sharp weight loss, suggesting the occurrence of substantial decomposition of the components of the composite, most likely the PP molecules and the compatibilizer used. The results clearly display that the higher the quantity of zeolite, the smaller the weight loss, which is a reasonable trend considering very high thermal stability of zeolite, as
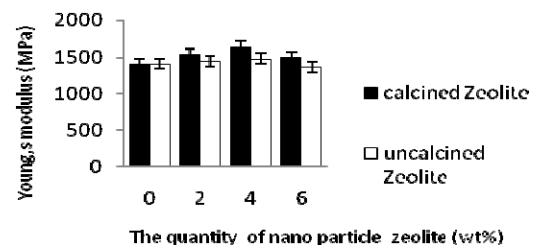
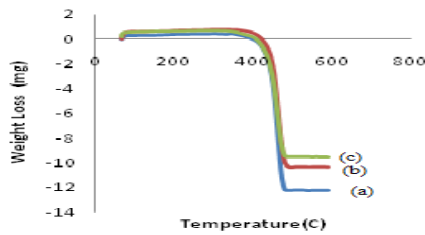**Figure 3. Young's Modulus of the Samples Reinforced with Uncalcined and Calcined Zeolite**

Figure 4. TGA Thermograms of the Samples Reinforced with Different Quantities of Uncalcined Zeolite, (a) 2 wt%, (b) 4 wt%, and (c) 6 wt%
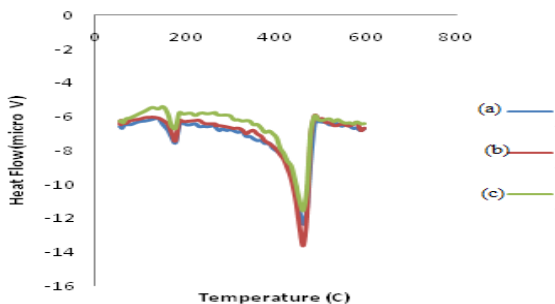

Figure 5. DTA Thermograms of the Sample Reinforced with Different Quantities of Uncalcined Zeolite, (a) 2 wt% (b) 4 wt%, and (c) 6 wt%

agreed with the results by other researches [11]. Overall, it can be seen that above 497 °C, no more weight loss was observed, reflecting that the composition of the samples have reached a stable state. As can be observed, the higher the amount of zeolite used, the larger the weight loss of the sample. This is a reasonable result since more zeolite particles suppress the decomposition of the molecules of PP and compatibilizer because the interaction of zeolite with the PP molecules strengthen the PP chains, making them more resistant to decomposition [10].

The corresponding DTA results presented in Figure 5 displays the existence of two endothermic zones, which supports the weight loss pattern as seen by TGA technique.

The first endothermic zones, located at around 170 to 180 °C, is assigned to the removal of trapped water and volatile components of the PP blend. Very prominent decomposition of the composite was very likely occurred at temperature around 450 to 500°C, as suggested by the very sharp endothermic zones. This endothermic zone suggested very substantial decomposition of the organic components of the composite and crystallization of zeolite, resulted in fixed thermal stability of the samples. This means that zeolite particles and polypropylene chain mixed homogeneously to form compact composite as a result of highest adhesion between PP and zeolite [10].

The TGA thermograms of the samples reinforced with different amounts of calcined zeolite are compiled in Figure 6 and the corresponding DTA results are presented in Figure 7.

Comparing the results obtained for the samples reinforced with uncalcined zeolite (Figure 4 and Figure 5) to those obtained for the samples reinforced with calcined zeolite (Figure 6 and Figure 7) it can be seen that thermal behaviors of the two sets of the samples are practically the same. This similarity reflects that uncalcined and calcined zeolite imparted similar effects in changing the thermal properties of the PP-zeolite composites. Both sets of samples were found to display two endothermic peaks, indicating the releases of trapped water and volatile components of the samples at low temperature at around 170 to 180 °C, followed by decomposition of more stable components at temperature around 450 to 500 °C, leading to formation of crystallized and stable composite. Further evaluation of thermal properties of the samples was carried out using DSC technique, with the main purpose to measure
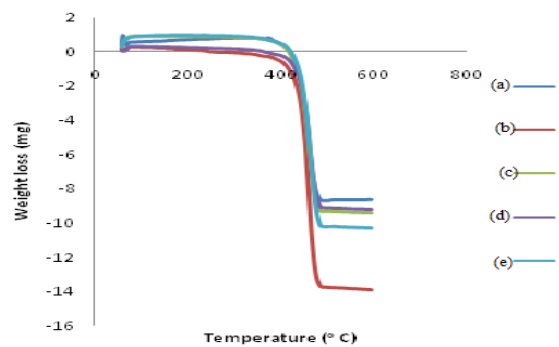

Figure 6. TGA Thermograms of the Samples Reinforced with Different Quantities of Calcined Zeolite, (a) PP, (b) 0 wt%, (c) 2 wt%, (d) 4 wt%, (e) 6 wt%
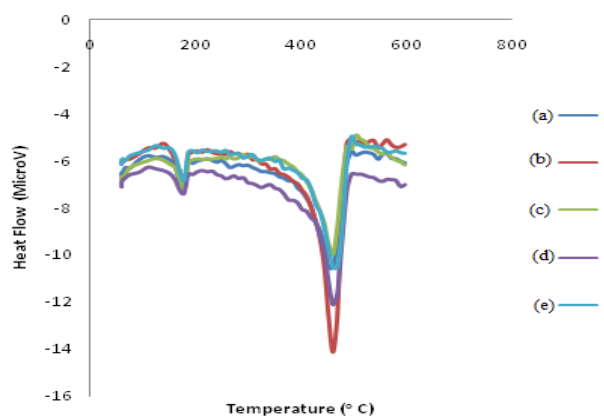

Figure 7. DTA Thermograms of the Samples Reinforced with Different Quantities of Calcined Zeolite (a) PP, (b) 0 wt%, (c) 2 wt%, (d) 4 wt%, (e) 6 wt%

melting point of the composite, which is not available from TGA and DTA technique. The results are presented in Figure 8 and Figure 9.

The main information gained from DSC analysis regarding thermal properties is the heat involved in thermal event as a function of time and temperature. The heat involved is commonly expressed in term of enthalpy, which is the amount of heat released or adsorbed by the sample during thermal treatment. The negative value of enthalpy means that the sample adsorbs heat, as indicated by the endothermic peak on the DSC thermogram. In addition, DSC analysis provides quantitative information about melting point and phase transition of the sample.

As can be seen in Figure 8 and Figure 9, all samples melt at practically the same temperature, but with different enthalpies. In general, it can be seen that for the two sets of the samples, the higher the amount of zeolite added, the higher the enthalpy of the sample. This trend is in agreement with high thermal stability of zeolite, and, therefore, the higher the amount of zeolite in the composite the more heat was required to melt the samples.

The results of thermal analyses for the samples reinforced with uncalcined zeolite are compiled in Table 2 and those for the samples reinforced with calcined zeolite are shown in Table 3. As can be seen in Table 2, the samples reinforced with uncalcined zeolite have

melting points ranging from 167 to 171 °C, with slight increase following the increased amount of zeolite added, which is in accordance with high melting point of zeolite. The effect of the amount of zeolit used on melting point is in agreement with the increase in decomposition temperature as can be seen Table 2, which ranging from 381 to 489 °C. The melting point and decomposition temperatures were found to decrease with increased amount of zeolites used, sugesting that the components of the samples decomposed were PP, while the zeolite remained intact. Overall, it can be seen that the melting points of the reinforced samples are higher than that of unreinforced sample, indicating that some of the heat was absorbed by the zeolite [22].

Comparing the data for the samples reinforced with calcined zeolite (Table 3) to those for the samples reinforced with uncalcined zeolite (Table 2), it can be seen that the effect of the amount of zeolite added is practically similar. It is also found that no significant different in the melting point of the samples reinforced with uncalcined and calcined zeolite at the same quantity. For the samples reinforced with calcined zeolite, the melting points ranging from 169 to 172 °C. The main difference observed is the slightly higher decomposition temperatures of the samples reinforced with calcined zeolite, which lies in the range of 379 to 497 °C, suggesting that the samples reinforced with calcined zeolites are more resistant to thermal decomposition.
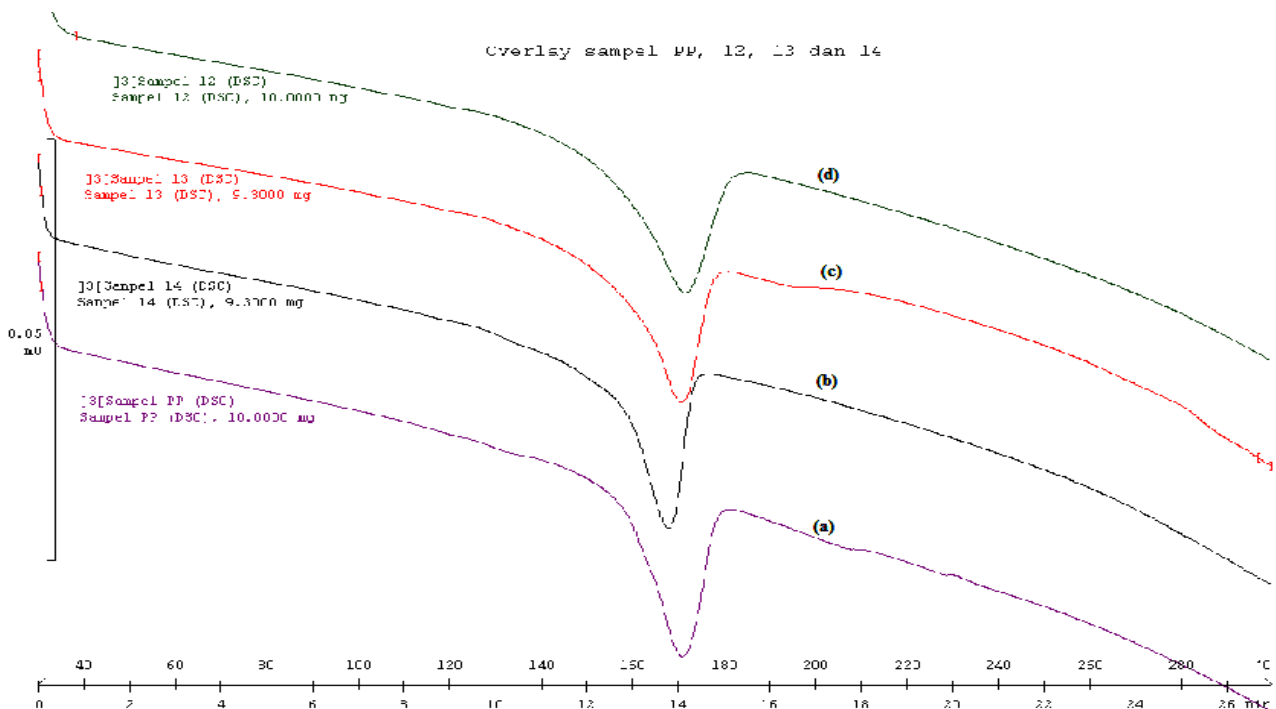

Figure 8. DSC Thermograms of the Sample as Reinforced with Different amounts of Uncalcined Zeolite, (a) 0 wt%, (b) 2 wt%, (c) 4 wt%, (d) 6 wt%
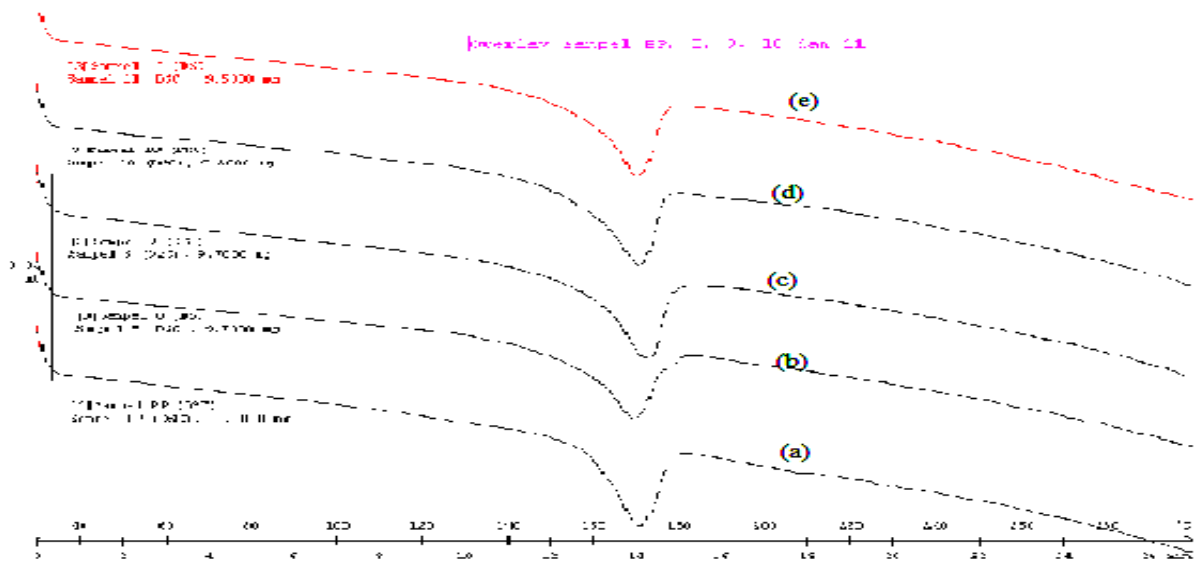
Figure 9. DSC Thermograms of the Sample as Reinforced with Different amounts of Calcined Zeolite, (a) pure PP, (b) 0 wt%, (c) 2 wt%, (d) 4 wt%, and (e) 6 wt%

Table 2. Thermal Characteristics of the Samples Reinforced with Uncalcined Zeolite

(wt%)	Melting point ($^{\circ}$C)	Decomposition ($^{\circ}$C)	Endothermic peak ($^{\circ}$C)	Mass varation (mg)	Mass Variation (%)	Enthalpy (mJ/mg)
2	170.80	385.07-489.07	463.03	-11.00	-61.77	-21.93
4	169.63	372.63-488.23	461.33	-12.53	-61.12	-21.65
6	166.90	381.23-487.63	458.10	-9.75	-58.03	-20.73

Table 3. Thermal Characteristics of the Samples Reinforced with Calcined Zeolite

(wt%)	Melt point ($^{\circ}$C)	Decomposition ($^{\circ}$C)	Endothrmic peak ($^{\circ}$C)	Mass variation (mg)	Mass variation (%)	Enthalpy (mJ/mg)
0	168.66	381.73-492.07	455.70	-9.34	-56.93	-20.04
2	171.55	378.93-489.87	460.47	-9.94	-62.94	-18.01
4	169.75	398.90-494.07	463.67	-8.88	-61.24	-18.39
6	169.09	397.90-497.10	464.10	-10.69	-58.44	-15.36

4. Conclusions

The results obtained clearly demonstrated significant effect of zeolite on mechanical and thermal properties of PP-zeolite composite. The results obtained clearly revealed that zeolite was able to significantly increase tensile strength and Young's modulus of the samples, with calcined zeolite found to work better. For elongation at break, addition of calcined zeolite was found to result in increased fracture elongation of the samples reinforced with zeolite up to 4 wt% but decreased sharply for the sample reinforced with 6 wt% zeolite, while for the samples reinforced with uncalcined zeolite, no consistent trend was observed. Thermal analyses demonstrated that the samples reinforced with calcined zeolite are more resistance to thermal treatment than those reinforced with uncalcined zeolite, as indicated by higher decomposition temperature of the samples reinforced with calcined zeolite. DSC analyses reveal that no significant difference of the melting points of the samples was observed, but the effect of the quantity of zeolite on enthalphy is quite evident, in which the higher the amount of zeolite added, the higher the entalphy of the composite.

Acknowledgement

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