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Preparation and Characterization from Natural Zeolite Sarulla of North Sumatera Polyurethane Nanocomposite Foams

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Abstract
Has made the manufacture of natural zeolite from the Sarulla, District Pahae, North Tapanuli North Sumatra Province in the form of chunks with the process of grinding to a size 200mesh (74μm). The natural zeolite refining and calcination process is carried out at a temperature of 600°C for 1 hour and without the process of purification and calcination and then processed into nano particles of natural zeolite with the ball mill for 21 hours. The method used in research on nanocomposite processing of polyurethane foam are: 1) Preparation of natural zeolite nanoparticles; 2) Preparation of nanocomposite made by mixing nano particles of zeolite in the mixture of PPG and TDI in the mold to room temperature at a rate of 100rpm for 30 seconds, with a composition of nanoparticles of natural zeolite (0%, 5%, 10%, 15%, 20% and 25%) wt; 3) Preparation of specimens for each sample testing in accordance with ASTM D 638 standard sizes for the dumbbell Type V tensile strength; and 4) The characters include: mechanical properties (tensile strength, elongation and modulus of elasticity) and morphological analysis by SEM. From the analysis of natural zeolite preparation obtained particle size 129,7nm for natural zeolite calcination, for natural zeolite without calcination obtained 95,8nm particle size. Results of the analysis of chemical constituents of natural zeolite nanoparticles obtained by calcining SiO_2 content of the element (70.98%) and Al_2O_3 (17:22%) while natural zeolite nanoparticles without calcination obtained element SiO_2 content (80.28%) and Al_2O_3 (14.21%). The influence of the quantity of filler PU / zeolite in tensile strength, elongation, and modulus of elasticity was found that the optimum concentration of filler is at 20%. Results of analysis of the morphology of nanocomposite polyurethane foam is homogenous and spread evenly. Results of XRD analysis of the natural zeolite is mordenite types.
Keywords: PPG, TDI, natural zeolite nanoparticles, mechanical analysis, FTIR analysis, and morphology analysis.

1. Introduction

Today many industry and academia to develop research on nanocomposite polyurethane foam. Polyurethanes are made by reacting molecules having isocyanate groups with molecules containing hydroxyl groups, so that the type and size of each molecule forming will give effect to the properties of the resulting polyurethane. This is what causes the polyurethane into one highly flexible polymer excellent in mechanical properties and application (Goud, et al., 2006).

Most polyurethane applications today is a foam material, followed by elastomers, adhesives and coatings. Today the study of polymers that can be used as foam materials have been developed because of the need for such polymers is increasing. Efforts to develop a polymer that can be used as a foam material put emphasis on the synthesis of new polymers that can be produced, and the basic ingredients are relatively inexpensive and easy to obtain.

The main challenge in the polymer industry is a way to improve the quality of existing products or create new products. Every day comes new and better products in terms of quality and price in the market. Likewise, the material is natural zeolite attention, because it has a distinctive character which is an inorganic compound of alumina silicate structure which has a three-dimensional framework consisting of silica (SiO_4) and alumina (AlO_4), and its structure has pores. Natural zeolites are minerals inexpensive and has become an important part in the polymer industry where its use as a filler material is very economical to modify and improve the performance of the material creation. There are many types of mineral, but zeolite has a long record as most inorganic materials are added as fillers into the polymer matrix (Wagener, et al., 2001; Rihayat, et al., 2007).

One engineering materials recently developed in Indonesia is nanotechnology. Royal Society of London in Arryanto, et al., (2007) defines nanotechnology as design, production, characterization and application of structures, devices and systems by controlling shape and size at the nanometer scale. In nanotechnology, materials can be designed according to the needs and desires. In addition, the efficiency and optimization of the material is also increased while the size of the nano (10^{-9}m). This occurs due to an increase in the properties and performance of materials engineered (Nuryadi, 2009).

From the above description, researchers interested in conducting research with the aim to increase the benefits of natural zeolite, and in this study is more focused to produce nanocomposite polyurethane foam with natural zeolite nano fillers. This modification also for the improvement of the natural zeolite, considering that this product has a source of raw materials with large amounts of area Sarulla, District Pahae, North Tapanuli, North Sumatra Province, so as to increase the income of local communities if there will be mass produced.

This study is the first step in the provision of technology/method is simple and relatively inexpensive in nanocomposite processing of flexible polyurethane foam and padded, and also to enhance the benefits of natural zeolite to produce nanocomposite foams polyurethane / nano natural zeolite.

2. Research Methods

2.1. Preparation and Purification Process Zeolite

At this stage, the natural zeolite Sarulla obtained from the District of Pahae North Tapanuli province of North Sumatra, natural zeolite is taken in the form of chunks in large measure, to make it in the form of small size in the nanometer size, then the process is carried out by steps as follows; to solve a large chunk, the first destroyed by using a hummer mill and then crushed using a mortar muller until smooth shape with a size of 200 mesh (74 micrometers). Preparation phase consists of crushing, until the milling. Before the process in a ball mill, a natural zeolite first crushed and crushed to a smaller size (roughly the size of sand) to facilitate the time of grinding to obtain a zeolite in the size of 200 mesh. This process is carried out in laboratories Polymer Chemistry University of North Sumatra, Medan. Natural zeolite with a size of 200 mesh performed purification and calcination process, it aims to improve specific properties of natural zeolite by removing the elements of impurities and evaporation of water trapped within the pores of zeolite crystals.

In the process of removing impurity substances present in the zeolite content of the activation process is carried out with the following steps; then to eliminate the levels of impurities such as Fe used magnets, to remove impurities Al conducted a chemical process using a solution of 0.05N HCl levels. The HCl solution in the mix into natural zeolite in a container with as much as 300ml, then stir until homogeneous using a magnetic stirrer for 1 hour at 70°C, then allowed to stand for one night. Then filtered using filter paper with the aim of separating HCl solution with natural zeolite and then laundering repeated using distilled water and re-separate the natural zeolite with distilled water to obtain a neutral pH. Activation zeolite chemically with the aim to clean the surface of the pores, removing impurities compounds and rearrange the location of the atoms can be exchanged. The activation process zeolite with HCl acid treatment led to zeolite dealumination and dekationisasi experience that the release of Al and cations in the zeolite framework. Dekationisasi acid activation causes that led to the increase of surface area of zeolite due to reduced impurity covering the zeolite pores. Increased surface area is expected to increase the ability of zeolite in the adsorption process. The high content of Al in the zeolite framework led to very hydrophilic zeolite framework. Hydrophilic and polar properties of zeolite is an obstacle in the ability penjerapannya. The activation process by acid can improve the crystallinity, acidity and surface area.

2.2. Nanoparticle Production Process Zeolite

Natural zeolite filter results that have been purified, dried first under the sun and then heated with a furnace at a temperature of 600°C for 1 hour, then the powder is stored in a desiccator until used for ball mill. Natural zeolite calcination and without calcining results in a size of 200 mesh was added to the planetary ball mill PBM-4 respectively for 21 hours, so that the natural zeolite obtained in nano size. Results of nano particles natural zeolite that has been purified and without purification then characterized to determine how big the size of the natural zeolite produced by the ball mill by using particle size analysis (PSA), as well as analysis of chemical constituents contained in nano particles of natural zeolite results calcination and without calcination by using XRF and crystal structure analysis by using XRD and morphological analysis by using SEM.

2.3. Process and Character nano composite Polyurethane Foam By mixing between PPG and TDI with Nano particles of natural zeolite

Results from the manufacture of nano particles of natural zeolite was then mixed with PPG and TDI. Percentage weight of PPG and TDI, namely: PPG: 60% wt and TDI: 40% wt. The percentage by weight of (%wt PPG, wt% TDI and wt% nano particles of the zeolite. Preparation by first mixing the nano particle zeolite with PPG and stirred using a mixer for 30 seconds at room temperature at a speed of 100 rpm (PPG + nano particles of the zeolite nature), then mixing the nano-particle zeolite with TDI and stirred using a mixer for 30 seconds at room temperature at a speed of 100 rpm (TDI + nano particles of natural zeolite). The mixture between (PPG + nano particles of natural zeolite) with (TDI + nano natural zeolite particles) are mixed together and stirring using a mixer for 30 seconds at room temperature at a speed of 100 rpm, to obtain a homogeneous mixture, then poured into a mold, and characterization. The percentage composition by weight of the zeolite nanoparticles can be seen in Table 2.1. below this.

Table 2.1. Ingredients Weight Percent Composition (% wt PPG, TDI and% wt% wt zeolite Nanoparticle)

No	PPG	TDI	Nanoparticles zeolite
1	60%	40%	0%
2	60%	40%	5%
3	60%	40%	10%
4	60%	40%	15%
5	60%	40%	20%
6	60%	40%	25%

3. Results and Discussion

3.1. Results Analysis of Nanoparticle Zeolite For Chemical Composition With XRF

Results of the analysis of the chemical composition of nanoparticles of natural zeolite without calcination (Table 2.1) and calcined natural zeolite (Table 2.2) can be seen below. In Table 2.1. it appears that the dominant compound is SiO_2, and Al_2O_3, while other compounds are impurities, whereas in Table 2.2, it appears that the dominant compound is SiO_2, Al_2O_3 and K_2O, while other compounds are impurities.

Table 3.1. Chemical Composition of Natural Zeolite Nanoparticle Without Calcination

Compound	Composition (% weight)
P_2O_5	0.60
Na_2O	1.76
MgO	0.12
Al_2O_3	**14.21**
SiO_2	**80.28**
K_2O	1.45
CaO	0.14
TiO_2	0.52
Fe_2O_3	0.92
Amount	**100.00**

Table 3.2. Chemical Composition of Natural Zeolite

Compound	Composition (% weight)
Na_2O	1.12
MgO	0.82
Al_2O_3	**17.22**
SiO_2	**70.98**
K_2O	4.62
CaO	1.91
TiO_2	0.51
Fe_2O_3	2.82
Amount	**100.00**

Nanoparticles Calcination

Nano particles of natural zeolite without calcination obtained Si/Al = 5.65, while the nano particles obtained by calcining natural zeolite Si/Al = 4.12. In the natural zeolite without calcination showed the density of Al atoms in the crystal framework structure is quite high. By calcination there are compounds that lost the P_2O_5, this is caused because the refining process with HCl and heating process at a temperature of 600°C, types of natural zeolite prepared is mordenite, the value of ratio Si / Al high will cause the mordenite has a thermal stability is high and not indicate any change in, to kind of mordenite ratio Si/Al = 4.17 to 10 (Chai Mee Kin, et al., 2001).

From the results of the research data in Table 4.1, for zeolite without calcination showed higher levels of Si which is equal to 80.28% compared to 70.98% by calcination, Si high-grade zeolite is hydrophobic and has affinity to hydrocarbons (Chai Mee Kin, et al., 2001), so expect natural zeolite nanoparticles are used as a filler material in the processing of polyurethane foam can be homogeneous.

3.2. Characterization of Particle Size Zeolite With PSA

Before nanozeolit used as filler in the manufacture of polyurethane foam, then nanozeolit obtained were characterized using PSA to know how big the size of the nanoparticles appropriately. Of the tool is obtained percent of the intensity distribution, volume distribution and number distribution.

Table 3.3. The test data zeolite calcination

Distribution Result (Contin)

Intensity Distribution			Volume Distribution			Number Distribution		
Peak	Diameter(nm)	Std.Dev.	Peak	Diameter(nm)	Std.Dev.	Peak	Diameter(nm)	Std.Dev.
1	155.7	18.3	1	141.1	15.2	1	129.7	12.5
2	0.0	0.0	2	0.0	0.0	2	0.0	0.0
3	0.0	0.0	3	0.0	0.0	3	0.0	0.0
4	0.0	0.0	4	0.0	0.0	4	0.0	0.0
5	0.0	0.0	5	0.0	0.0	5	0.0	0.0
Average	155.7	18.3	Average	141.1	15.2	Average	129.7	12.5

Table 3.4. The test data of natural zeolite without calcination

Distribution Result (Contin)

Intensity Distribution			Volume Distribution			Number Distribution		
Peak	Diameter(nm)	Std.Dev.	Peak	Diameter(nm)	Std.Dev.	Peak	Diameter(nm)	Std.Dev.
1	93.2	10.2	1	99.3	9.8	1	95.8	9.3
2	0.0	0.0	2	0.0	0.0	2	0.0	0.0
3	0.0	0.0	3	0.0	0.0	3	0.0	0.0
4	0.0	0.0	4	0.0	0.0	4	0.0	0.0
5	0.0	0.0	5	0.0	0.0	5	0.0	0.0
Average	93.2	10.2	Average	99.3	9.8	Average	95.8	9.3

Table 4.5. Differences Intensity Distribution, Distribution Volume and Amount Distribution nanozeolit nature with and without calcination

No	Process	Intensity Distribution (nm)	Distribution Volume (nm)	Amount Distribution (nm)
1	Calcination	155.5	141.1	129.7
2	Without Calcination	93.2	99.3	95.8

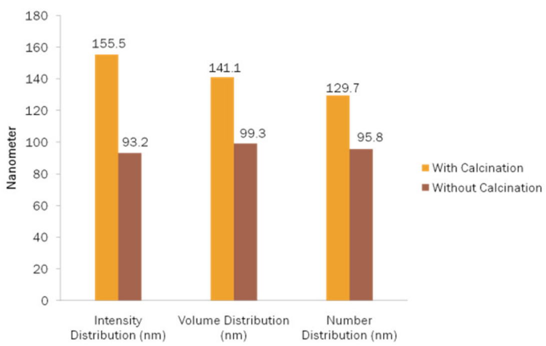

Figure 3.1. The difference in intensity distribution chart, Volume Distribution Amount Distribution and natural nanozeolit with and without calcination

3.3. Nanoparticle morphology Zeolite Without calcination and calcination

The form of nano particles calcined natural zeolite were observed by SEM are shown in Figure 3.2. From Figure 3.2 shows the surface of the zeolite has a crystal lattice in the form of surface pores of zeolite, it is in line with reports of zeolite crystalline solid microporous hollow and grooved and has a pore size of 3 to 10A-called molecular sieves (Liang and Ni, 2009). From the SEM photograph shown that dark colors are pores or cavities whose size <5 microns, and a bright color is a natural zeolite nanoparticles, when seen from the particle size then this is the kind of zeolite mordenite as particle size > 50nm.

In Figure 3, shows the results of SEM and EDX for nano particles natural zeolite without calcination, the composition of the dominant similar to the results shown on the data XRF, from images seen happen algomert or clumping, it is because zeolites are hydrophilic (readily absorbs water) because of the OH group at around the pores, as well as uneven distribution of particles with particle size of 95.8 nm.

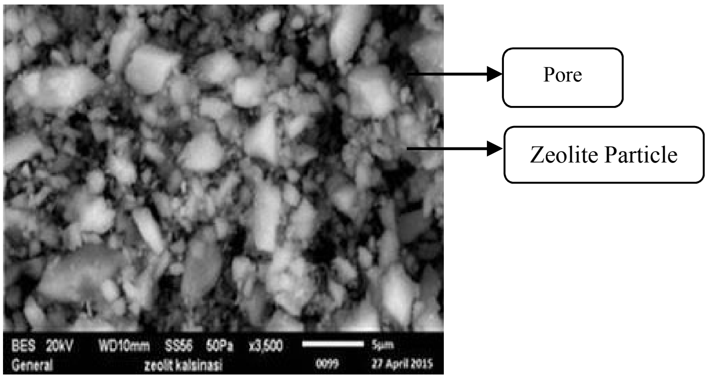

Figure 3.2. Nano-particle morphology of natural zeolite calcination enlargement 3500

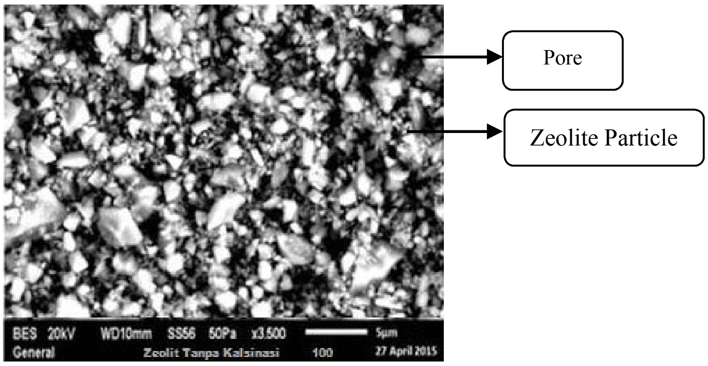

Figure 3.3. Nano-particle morphology of natural zeolite without calcination enlargement 3500

3.4. Results of XRD analysis Nanoparticle Natural Zeolite

Characterization XRD used in room temperature by using the tool Shimadzu XRD 600 X-ray diffractometer (40 kV, 30 mA) by using nickel for filtering radiation Cu Kα where the count rate (scanning) used is of 20 / min in the range (range) 2θ = 5-750.

Table 4.6. Results of X-ray Diffraction Analysis of Nano particles of natural zeolite without calcination

Corner (2θ)	D (Å)	I/I1	FWHM (deg)	Intensity (Counts)	Integrated Int (Counts)
29.7601	2.99965	100	0.12470	390	2523
27.6717	3.22111	84	0.26930	328	3886
27.9200	3.19303	52	0.15520	202	1606

The characterization results provide diffraction pattern shown in the display Figure 3.4 below.

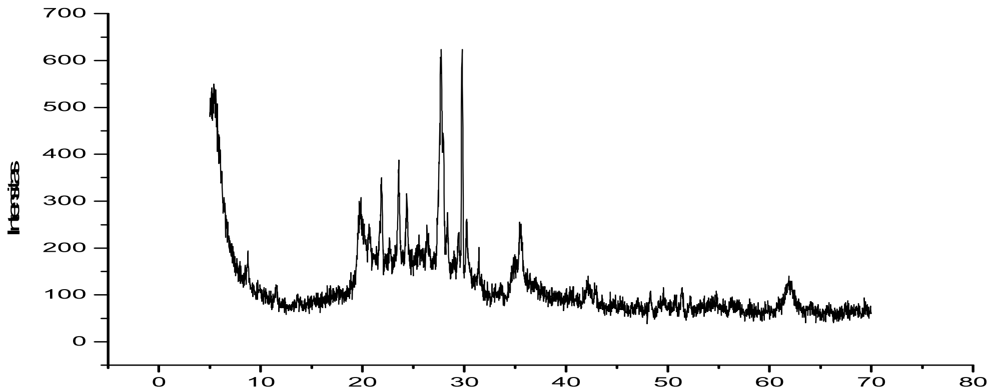

Figure 3.4. X-Ray Diffraction spectrum natural Zeolite

No. Card	Chemical Formula / Chemical Name (Mineral Name)	S	L / Dx	d / WT%	I / S.G.	R
1 13-0135	CaAl2Si10O24.7H2O / Calcium Aluminum Silicate Hydrate (Morden)	0.242	0.933(14/17) / —	0.847 / —	0.532 / —	0.421
2 29-1487	Al2O3 / Aluminum Oxide (Corundum, Syn)	0.209	1.000(7/7) / —	0.724 / —	0.554 / —	0.401

Diffraktogram of natural zeolite results in Table 4.6 shows the intensity at an angle 2θ = 29.76; 27.67; and 27.92. There is a maximum peak at an angle of 2θ = 29.76 with a distance of 2.99Å with a FWHM sepasi 0.124. These results compared to the standard diffraktogram mordenite zeolite types in Figure 4.8. Modernit standards provide a high intensity at an angle 2θ at 27; 25.63; 23 of these comparisons where the raw materials of natural zeolite obtained from the Sarulla, District Pahae, North Tapanuli, North Sumatra Province is a mordenite zeolite mineral species ($CaAl_2Si_{10}O_{24}.7H_2O$).

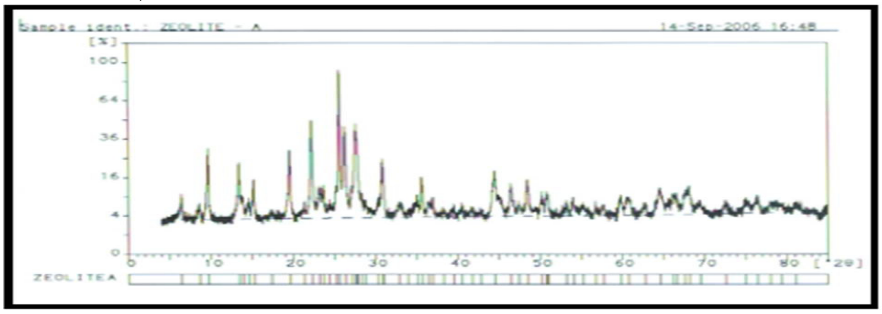

Figure 3.5. X-ray diffraction spectra of mordenite zeolite (MOR) as Standard

3.5. Preparation and Characterization of Polyurethane Foam nano composite filler

With Natural Zeolite Nanoparticles Processing nanocomposite polyurethane foam prepared with a ratio of fixed (constant) mixture of PPG and TDI (60%: 40%), and varied with the addition of natural zeolite nanoparticles composition (0-25)% wt. Results of nanocomposite preparation of polyurethane foam then dikarakter by using FTIR, SEM, and Strong Pull Test.

3.5.1. Results Analysis of Mechanical Properties (Tensile Strength (σt), elongation (ε) and Modulus of Elasticity nanocomposite foams Puliuretan)

One commonly tested mechanical properties of polymer compounds and materials are include tensile strength, elongation, and elasticity. Value analysis of tensile strength, elongation and elasticity nanocomposite polyurethane foam PPG polymerization results with TDI and nano zeolite particles with varying mixing ratio is an important factor to determine the mechanical properties of the desired material. Results obtained from testing Load and Stroke. Load price in units of kgf and stroke in mm. Results of this test is reprocessed to obtain the tensile strength (σt), elongation (ε) and elasticity.

3.5.1.1. Analysis Results Modulus of Elasticity nanocomposite foams Puliuretan mixture PPG / TDI / Nanoparticles of natural zeolite

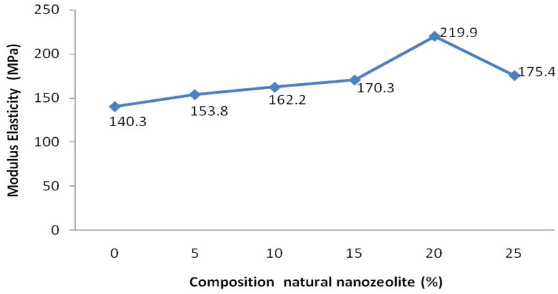

Figure 3.6. Graph the modulus of elasticity of the composition of nano particles of natural zeolite (0–25)% wt

Modulus of elasticity states strength of a material. The strength of a material is influenced by its constituent chemical bonds. Strong chemical bonds depends on the number of molecular bonds and bond types (such as covalent bonds, ionic bonds, hydrogen bonds and Van der Waals forces). Strong chemical bonds difficult to cut because it requires considerable energy to break the bond.

Figure 4 shows the relationship of the modulus of elasticity of the composition of the natural zeolite nanoparticles obtained from tensile testing machine, the information obtained from these images that the optimum value contained in nano-particle filler material 20% natural zeolite obtained a value of 219,9MPa.

By increasing the composition of nano particles of natural zeolite, modulus of elasticity is increasing, but the composition of the 25% modulus of elasticity decreases, favorable conditions obtained in mixed conditions PPG / TDI with nano particles of natural zeolite in the composition of 20% wt, with a filler in size nano then mix between PPG / TDI is more homogeneous and elastic. An increase in modulus of elasticity due to the natural zeolite is possible due to the nature of the natural zeolite has silicate layers in nanometer-sized natural zeolite can be dispersed homogeneously and evenly that give structure to the nanocomposite exfoliation. Silicate layers are dispersed individually have a large surface contact area so that it can bind strongly to the matrix PPG / TDI hereinafter effect on increasing the modulus of elasticity. The incorporation of nano particles of natural zeolite is more than 20% wt contrary negative effects that lower the modulus of elasticity.

3.5.1.2 Analysis Tensile Strength nanocomposite foams Puliuretan mixture PPG / TDI / Nanoparticles of natural zeolite

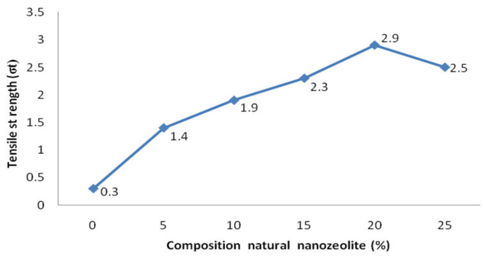

Figure 3.7. Graph tensile strength of the composition of natural zeolite nanoparticles (0 – 25)% wt in the nano composite polyurethane foam

Based on the measurement data shows that the mechanical properties of tensile strength at the best polyurethane foam in polyurethane foam with the addition of nanozeolit much as 20% which is equal to 2.9MPa. This is probably due to the silicate layers in nanometer-sized natural zeolite can be dispersed randomly and evenly giving exfoliate the nano composite structure. Silicate layers that exist in scattered individual zeolite has a large surface contact area so that it can bind strongly to the matrix PPG and TDI which further gives effect to the increase in tensile strength.

The incorporation of nano zeolite is more than 20% wt contrary negative effect that lowers the tensile strength but greater if no filler nanoscale zeolite particles. This is because the addition of 20% wt, mix the two components achieve harmony and improve the mechanical properties, in other words between the components reach equilibrium. On the composition of more than 20% wt cause disturbed the harmony of both components and produce poor physical properties. Mixing polyurethane-zeolite with a low level of mechanical properties have changed, although not yet reached the maximum level.

Filler particle size small increase Darajat reinforcement of polymers compared to large particle size (Leblance, 2002). The particle size has a direct relationship with the surface area per gram of filler. Therefore, small particle size provides a large surface area for interaction between the polymer matrix and filler material so increasing the reinforcement of polymeric materials. In summary, the smaller the particle size, the higher the interaction between the fillers and the polymer matrix. Kohls and Beaucage (2002), reported the results of his research stating that the surface area can be enhanced with the surface of the shaft or cavity on the surface of the charger. It is possible that the polymer can penetrate into the surface of the shaft when the mixing process. Particles dispersed homogeneously improve interactions through the adsorption of polymer on the surface of the filling material. Instead, the particles are not dispersed homogeneously may produce agglomerates or clots in the polymer matrix. Kewujudan agglomerates reduce the surface area so weaken the interaction between filler and matrix and result in a decrease in the physical properties of polymer materials.

Bussaya Rattanasupa and Wirunya Keawwattana (2007), conducted research using a mixture of polypropylene and natural rubber filler 50 phr natural zeolite with a particle size of 45µm was obtained tensile strength of 2,73MPa smaller when compared to the size of the nano-particles of zeolite for 95,8nm, this is because the smaller the particle size causes more homogeneous mixture.

3.5.1.3. Analysis elongation nanocomposite foams Puliuretan mixture PPG / TDI / Nanoparticles of natural zeolite

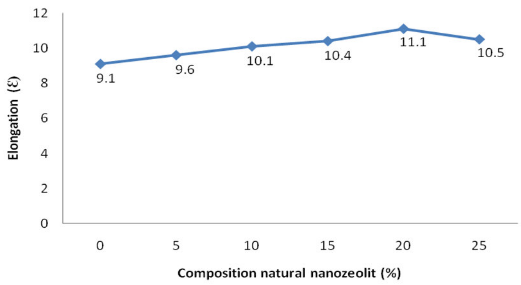

Figure 3.8. Elongation graph of the composition of the natural zeolite nanoparticles (0%, 5%, 10%, 15%, 20%, and 25%) in the nanocomposite polyurethane foam

Based on the measurement data shows that the mechanical properties of the polyurethane foam elongation at most good in polyurethane foam with the addition of zeolite nanoparticles as much as 20%, amounting to 11.1%. But the addition of the zeolite nanoparticles as much as a 25% decrease which amounted to 10.5%. This elongation decline due to limited movement of the molecular chains of the polymer due to the natural zeolite particles are rigid so that the value of elongation at break of commensal low. Ray appropriate research and Okamoto (2003), the addition of fillers to be impacting on the extension properties of the composite.

4. Conclusions

From the results of making and character nanocomposite filler polyurethane foam with natural nanozeolit Sarulla obtained several conclusions: preparation of nano particles of the zeolite can be made from natural zeolite Sarulla as filler in polyurethane foam, zeolite characterization results indicate that the particle size of zeolites (95,8nm), XRD and XRF analysis showed that the type of zeolite used is mordenite, composition ($CaAl_2Si_{10}O_{24}.7H_2O$) for calcined zeolite is predominantly Al_2O_3 (17.22%) and SiO_2 (70.98%) whereas for zeolite without calcination dominant is on Al_2O_3 (14.21%) and SiO_2 (80.28%), preparation of polyurethane foam can be added with natural zeolite nanoparticles Sarulla, the polyurethane foam without adding zeolite shows where the thermal properties at temperatures up to 376.43ºC 316,63°C degradation of polymer chains to decompose at a temperature of 500°C, and the polyurethane foam with zeolite showed that the thermal properties where the temperature until the temperature 379.35°C 336,51°C degradation of the polymer chain to decompose at a temperature of 600°C. Properties of tensile strength, elongation, and modulus of elasticity that is best at 20% addition of zeolite nanoparticles in the amount: 2.9 MPa, 11.1%, and 219,9MPa.

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