

Sentani Natural Zeolite as a Filler for Polyethylene Composite

Tiurlina Siregar¹, Bambang Ari Wahjoedi²

¹Department of Mathematics and Natural Sciences, Faculty of Teachers Training and Education Cenderawasih University. Jl Raya Abepura Sentani, Jayapura, Indonesia

²Chemistry Department, Faculty of Mathematics and Natural Sciences, Bandung Institute of Technology, Bandung, Indonesia

Abstract- Background: Sentani is a district in the southern part of Jayapura, Papua, Indonesia. This district rich of zeolite that is mostly consist of mordenite (CaNa_2K_2) $\text{Al}_2\text{Si}_{10}\text{O}_{24}$ with degree of crystallinity of 53.14% (analyzed with X-R Diffractogram).

Polyethylene composite with natural zeolite fillers will have a high hardness, so it can be used as a rigid and hard plastic packaging.

This study aimed to analyze zeolite-polyethylene composite which is could be used as plastic pipes and exterior blinds which has the characteristics of weather resistant and high hardness.

Methods: Zeolite-polyethylen composite was prepared by blending polyethylene with natural zeolite as filler. The composition of zeolite used was varied from 1 to 65% w/w polyethylene. The zeolite grain size – 150 + 200 mesh was blended at 188°C for 8 minutes. Every composition was analyzed its strength, hardness and weather resistant to find the best composition.

Results: The composite has tensile strength of 21.223 MPa (yet, the standard use elongation of matrix without filler is 3.0 – 3.3 MPa). The tensile test showed the relationship between tensile strength and composition of composite. The tensile strength was increasing with the addition of zeolite. However it was decreasing at the addition of zeolite more than 55%.

The hardness measured with Vickers-hardness (HV). Standard hardness is 29.5 – 40.6 HV. The more zeolite used as filler the more hardness of the composite. In this study showed that with composition of 65% zeolite the hardness yielded 41.1 HV.

The weather test conducted over 16 weeks in open air. The test showed that the composite with 55% zeolite filler was not degraded after 16 weeks of exposure compared to polyethylene alone.

Conclusion: Polyethylene composite with natural zeolite fillers of 55% has a high quality of hardness, elongation and resistant to weather. This composite is suitable for pipe and exterior blinds.

I. BACKGROUND

The growing demand of plastic material, especially for industry and households required innovation to create new materials that fit the demand, for example, a material that is known as a composite polymer (gas membrane, electrolyte membrane, fuel cells).

The composite material consists of a matrix material which is a combination or combinations of two or more different

materials. The combination forms a new material with specific material characteristics. Materials that could be particles, fibers, laminar and others. Matrices used in the manufacture of composite materials in general are polymers [1].

The use of polymers as matrix gives an advantage in the manufacturing process because it has a low density. The polymers are often used as the matrix is polyethylene (PE), polyvinyl chloride (PVC), polypropylene (PP) and polystyrene (PS).

The wide use of polyethylene due to two reasons those are the abundant availability and the price compared to the other polymers. In addition, polyethylene has a tensile properties, stiffness, a low degree of crystallinity, rust resistant, elastic and resistant to acid at room temperature (25°C) [2]. In the diversified use of polyethylene usually modifications were done to improve the properties and structure by adding additives for filler and reinforcement [3].

Zeolites are hydrated aluminosilicate crystal containing alkali and alkaline earth elements [3, 4].

The empirical formula of natural zeolite is $\text{M}_{2/n}\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{X}(\text{SiO}_2)_y \cdot \text{H}_2\text{O}$

M = alkali or alkaline earth cations

N = valent cations

X = the amount of silica

y = function of porosity

According to the geochemical and mineral structure, natural zeolite is a frozen volcanic products. Based on the process of its formation, natural zeolites can be classified into three groups 1). Zeolites which are derived from volcanic rocks, generally have a complex physical and chemical properties and contain many types of phillipsit, faujasite, mordenite, stillbit and gmelnit. 2). Zeolite derived from sedimentary rocks. This type usually has a very small grain size. 3). Zeolites from metamorphic rock and metasomatik rock [4-6].

In Sentani (Papua) could be found a precipitated zeolite deployment approximately 4.84 acres with an average thickness of about 5 meters. Sentani zeolites are tuffaceous in characteristic, with a greenish color (Figure 1). At this time the utilization of natural zeolite relatively large, for example, used in agriculture, animal husbandry, industry, and others.

According to Didik [7], mordenite type zeolite is used as filler in papermaking, because of its intra-crystallin pores (nature shaft) are easily achieved through its rings and channels. The type and amount of filler in polymer composite materials will affect the properties of the composite such as hardness, tensile strength and elasticity [8]. Fillers those are added into

polyethylene matrix in plastic industry could improve the quality of products [2]. A plastic material with some certain additive materials give some advantages, such as lightweight, strong and malleable, corrosive and chemicals resistant [9]. In addition, Hidenori Yahiro [10] considered the used of polytetrafluoroethylene-zeolite composite as gas membranes. To this end, this study aimed to analyze the characteristics of zeolite-polyethylene composite.

II. METHODS

1. Zeolite preparation

Zeolite was taken randomly from Sentani district, Jayapura regency, Papua. The zeolite sample was then soaked in 1 M HCl to eliminate micro-organisms. The clean zeolite was then heated at 110°C for 3 hours, dried, crushed using jaw crusher follow with roll crusher. Finally the zeolite was sieved to obtain the grain size of -150 - +200 mesh [11].

The natural zeolite was analyzed using X-ray diffraction (XRD) and Cullity equation to find the degree of crystallinity [12]

$$X_c = \frac{\text{Crystalline mass}}{\text{Crystalline mass} + \text{Amorf mass}} \times 100\%$$

2. Composite preparation

Polyethylene in the form of seed crystals incorporated into plastomil flask. Natural zeolite then added (1 to 65% of polyethylene weight) and mixed well at 188°C for 8 minutes. The signal from the plastomil instrument illuminates when the perfect mixture achieved.

3. Filming

Composites as much as 1.7355 g was placed in a 20 x 20 cm glossy stainless steel plate and covered with other glossy stainless steel plate of the same size. The temperature was set to 150°C and subsequently pressed in hot conditions with burden of 3.5 ton for 3 minutes. The study was conducted twice for every weight variation of the zeolite.

Study area:

The study was carried out at Sentani district, Jayapura regency, Papua province, Indonesia. Sentani is located at 02°33'S, 140°33'E southern part of Jayapura city which is the capital of Papua province. The district is located in low land area 88 m above sea level. The climate and weather are homogeneous all over Sentani [13].

Composite analysis:

The composite was analyzed for its hardness, tensile strength and weather resistant.

1. Tensile strength test

Seven samples were printed according to ASTM-D-638 standard (Figure 2). Each sample of composition has a different weight of zeolite. Using autograph samples were stretched to break to find the tensile strength.

2. Hardness test

Samples size of 1.5 x 2.0 x 8.0 cm with different zeolite composition was tested for their hardness according to Vickers-hardness (HV).

3. Weather test

Fifty five percent zeolite composition and control (0% zeolite) were exposed to the open air for 16 weeks to observe their colour changing.

III. RESULTS

The degree of crystallinity of the Sentani natural zeolite analyzed using X ray diffraction (XRD) and Cullity equation (Table 1) [14]. The XRD showed that the majority of natural Sentani zeolite contained of mordenite (CaNa_2K_2) $\text{Al}_2\text{Si}_{10}\text{O}_{24}$ and few feldspar (Figure 3).

The polymer composite of Sentani natural zeolite and LDPE was made in a plastomil with a various weight of zeolite (1 – 65% weight of LDPE) forming a light grey to dark grey plastic. The density of composite composition is shown in Table 2. There was no influence of zeolite weight to its density and there was no influence of LDPE weight to its density as well. This condition happened because of no mixing occurred. However, there was a changing in composite density. The higher percentage of zeolite caused the higher density of the composite [15].

The tensile test was conducted to determine the mechanical properties of the material before and after addition of zeolite. The test performed seven times for each composition. The strength at break (τ) of the composite was determined by multiplying the gravity (g) with average of breaking force (F). ($\tau = Fg$). Similarly, the tensile strength (σ), determined by divided strength at break (τ) with the average area of sample (A). ($S = \tau/A$). Finally the breaking elongation (C) determined using formula $C = \Delta l/l$. (Δl = Number of elongation and l = Intensity). Table 3 together with Figure 5, 6 and 7 showed the tensile strength of the composite.

The hardness of the composite measured in Vickers standard (HV). Table 4 and Figure 8 showed the result of the test. The more zeolite added to the LDPE the harder the composite, because the increasing interaction between zeolite and LDPE [2].

The weather test conducted in 16 weeks. The composites (55% zeolite and LPDE) were exposed to the open air and compare to control which was 0% zeolite and LPDE. The result was shown in Figure 9.

Compare with control, after 16 weeks the composite was not deteriorating (indicating by the colour changing). For this purpose, the composite could be used as raw material for plastic pipes and exterior blinds.

IV. DISCUSSION

The degree of crystallinity of natural zeolite shown in Table 1. This degree described the percentage of zeolite in the sample. This study showed that the degree of crystallinity (X_c) was 53.14% which was lower than the crystallinity of polymer Low Density POLYETHYLENE (LDPE) which was 60-65 % [8]. In the polymer material, the smaller the degree of crystallinity the greater the elasticity, this is due to the adding of the branch chains. The more branch chains occurred, the more elastic the material. However, the addition of lower crystallinity zeolite will not increase the elasticity of the composite.

Table 2 described the density of the zeolite. The higher percentage of zeolite caused the higher density of the composite.

Zeolite contained of Si (IV) and Al (III) which is bound with Oxygen to form an anionic chain with a number of negative charges proportioned to the amount of aluminum. The negative charge is neutralized by the positive ions which are located in the outside channel of the chain. The number of molecules could go inside the zeolite pore limited to the diameter of the pore and controlled by the number of positive ions.

Polyethylene having a long C-H chain. Accordingly, $O^{\delta-}$ on zeolites and $H^{\delta+}$ on LDPE bound each other by the London force or dispersion force (force due to the uneven distribution of $O^{\delta-}$ and $H^{\delta+}$ electrons) [4]. The interaction between LDPE and zeolite is shown in Figure 4.

Indeed, the polymer will fill all the zeolite cavities with a strong bound and consequently produce a much stronger composite than the polymer itself.

Figure 5 showed that the strength at break increased in addition of zeolites as filler (1-55%). This condition caused by the great attractive forces between LDPE atoms and zeolite. Hence, the addition of zeolite more than 55%, will decrease the strength at break. As commonly happens, this is due to the attraction or interaction between atoms dominated by the zeolite. The same explanation will go for the tensile strength. The addition of zeolite less than 55% will increase the tensile strength, but the strength will decrease in more addition of zeolite (Figure 6).

The breaking elongation was shown in Figure 7. The rigidity of the composite will increase parallel to the addition of zeolite. This is due to increasing interaction between bounded atoms (LDPE with zeolite). Yet, the addition of zeolite over 55% caused the attraction between the bounded atoms dominated by zeolite resulting the composite more rigid [2].

The composite (Sentani natural zeolite and LDPE) has a tensile strength more than 21.223 MPa which was higher than LDPE alone (3.3 MPa). In addition its hardness and breaking elongation was 40.7 HV and 1.29 MPa respectively. The standard for hardness and breaking elongation are 29.5 – 40.6 HV and 3.0 – 3.3 MPa [2, 16]. Therefore this composite was convenient to use as a raw material for plastic industry.

In the hardness test the composition of 55% zeolite has 40.7 HV. The more zeolite added to the LDPE the harder the composite, because the increasing interaction between zeolite and LDPE [2]. Therefore, the composite is considered could be used as a raw material for insulator plastic and film industry.

The 16 weeks weather test showed that the composite resistant to open air. Compare with control, after 16 weeks the composite was not deteriorating (indicating by the colour changing). It was considered that the interaction between zeolite and LDPE was not only happened in its C-H chain but also in other atoms. For this purpose, the composite could be used as raw material for plastic pipes and exterior blinds.

V. CONCLUSIONS

Natural zeolite mineral in districts Sentani, Papua consists of mordenite ($CaNa_2K_2$) $Al_2Si_{10}O_{24}$ with the degree of crystallinity of 53.14%.

An optimum composite material made of 55% Sentani natural zeolite and polyethylene (LDPE as Matrix) produce an optimum composite composition.

The composite analysis showed: the strength at break ≥ 16.887 MPa, tensile strength ≥ 26.369 MPa and breaking elongation ≤ 1.331 MPa. The composite has 16 weeks weather resistant.

We propose this composite for used as material in making pipe and exterior blinds.

AUTHORS' CONTRIBUTIONS

All the authors participated significantly in the analysis, drafting of the manuscript and writing the final version of the paper. TS conceptualized the study. BAW contributed towards the analysis.

ACKNOWLEDGEMENTS

Many thanks go to Prof Dr Siti Rochani for implementing the survey. We would also like to thank the Ministry of Research for sponsoring and funding this study.

REFERENCES

- [1] Thamzil L, Zamroni H: Penggunaan Zeolit dalam Bidang Industri dan Lingkungan. *Jurnal Zeolit Indonesia* 2010, 1 No 1.
- [2] Cowd MA: *Kimia Polimer*. Bandung: ITB; 2005.
- [3] Ibrahim A: *Introduction to Structural Steel Design*. 3 edn. Maryland: Department of Civil and Environmental Engineering; 2008.
- [4] Mainwaring DE: *The Nature of Zeolites and Their Role in Catalysis*. Melbourne: CSIRO; 2006.
- [5] Suminta S: Karakterisasi Zeolit Alam dengan Metode Difraksi Sinar-X B. *Jurnal Zeolit Indonesia* 2006, 5 No.2:5-7.
- [6] Glauco G, Ermanno G: *Natural zeolites*. Michigan University: Springer Verlag; 2010.
- [7] Didik F: *Zeolit Mineral Abad 21*. Bandung: ITB; 2002.
- [8] Weidmann G: *Structural Material Great Britain*. London; 2006.
- [9] Imam M: Sifat dan Karakteristik Material Plastik dan bahan Adiktif. *Traksi* 2005, 3 No. 2:7-9.
- [10] Yahiro H, Konda Y, Yamaura H, Okada G: Study on Zeolite/Poly(tetrafluoroethylene) Composite Membrane for Application to Fuel Cell. *Departemen of Applied Chemistry* 2003, 790-8577:60-65.
- [11] Siregar T: Penggunaan Zeolit Alam Sentani Sebagai Pengisi bahan Komposit Polietilen. *Jurnal Tekmira* 2014, 10 No 1:22-31.
- [12] Cullity BD: *Elements of X-Ray Diffraction*. 3 edn. Indiana: Addison Wesley; 2007.
- [13] BPS: *Papua in Figure*. BPS-Statistics of Papua Province; 2010.
- [14] Leslie H: *Composites Materials*. New York: Elsevier Publishing Company; 2006.
- [15] Yao YG, Zhu YF: The Influence of Surface Cross- Linking of the High Density Polyethylene Induced by Plasma Treatment Efficiency. *Journal Of Polymer Science* 2003:57-65.
- [16] ORNL: *Application to Fusion and Generation IV Fission Reactors*. In *Workshop on Advanced Computational Materials Science*; 2004.

AUTHORS

First Author – Tiurlina Siregar, Department of Mathematics and Natural Sciences, Faculty of Teachers Training and Education Cenderawasih University. Jl Raya Abepura Sentani, Jayapura, Indonesia, Email: tiurlina.siregar@yahoo.com

Second Author – Bambang Ari Wahjoedi, Chemistry
Department, Faculty of Mathematics and Natural Sciences,

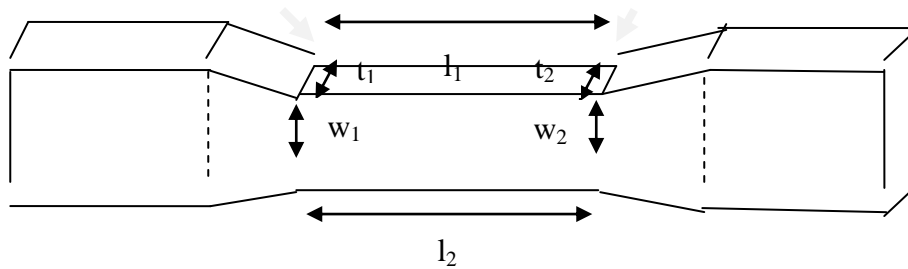
Bandung Institute of Technology, Bandung, Indonesia, Email:
bambang.ariwahjoedi@petronas.com.my

Figures

Figure 1 - Sentani Natural Zeolite, Papua



Figure 2 - Specimen according to ASTM D-638



l = length

w = width

t = thick

Figure 3 - XR Diffractogram of Sentani Natural Zeolite

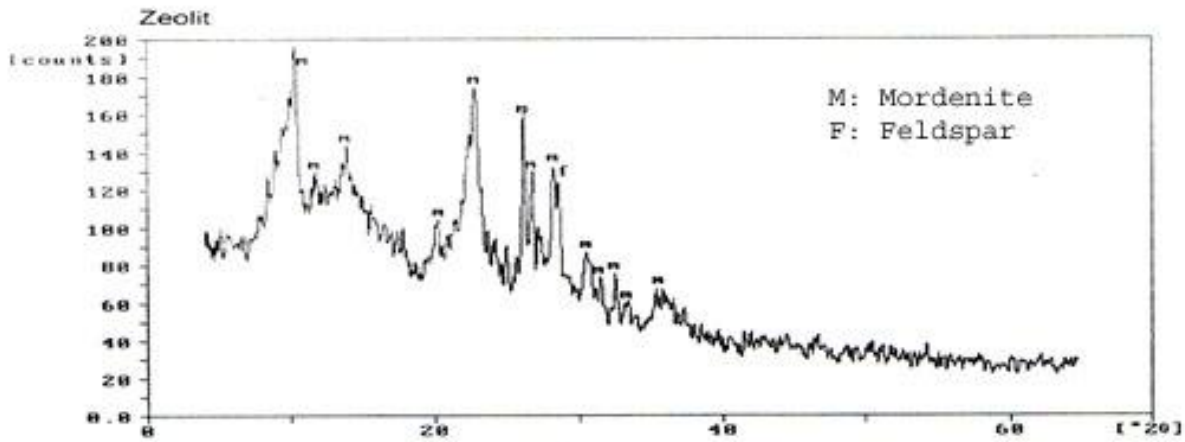


Figure 4 - Interaction between Natular Zeolite and LDPE

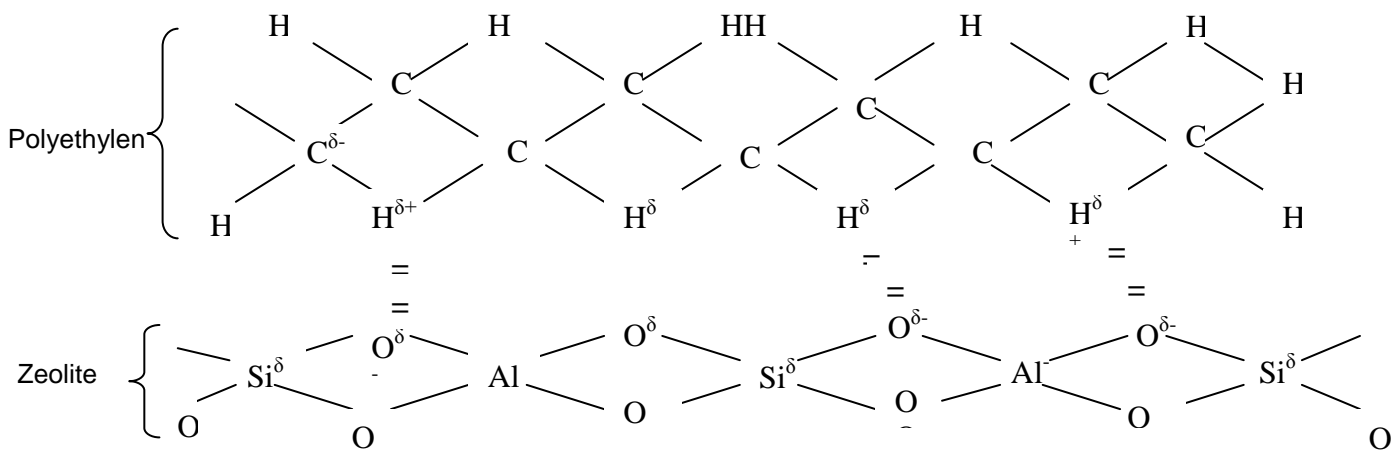


Figure 5 - Composite composition in relation with strength at break

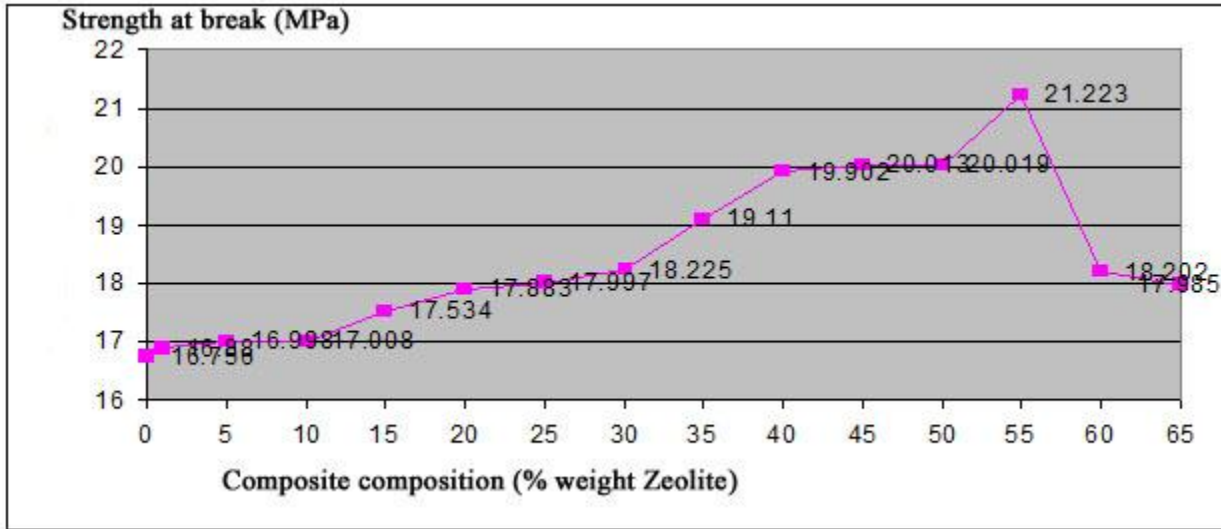


Figure 6 - Composite composition in relation with tensile strength

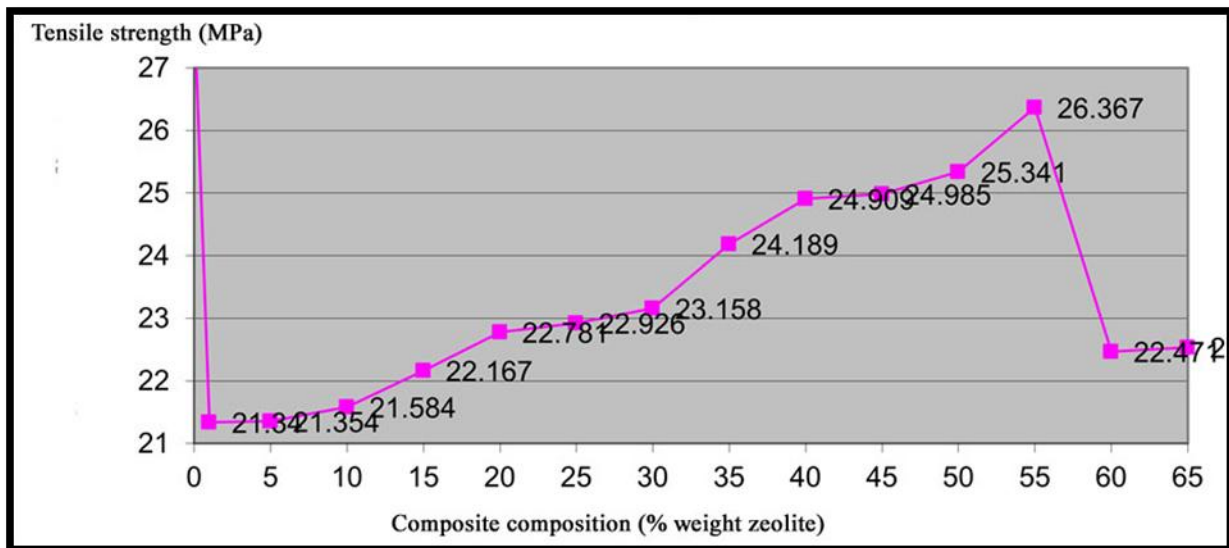


Figure 7 – Composite composition in relation with breaking elongation

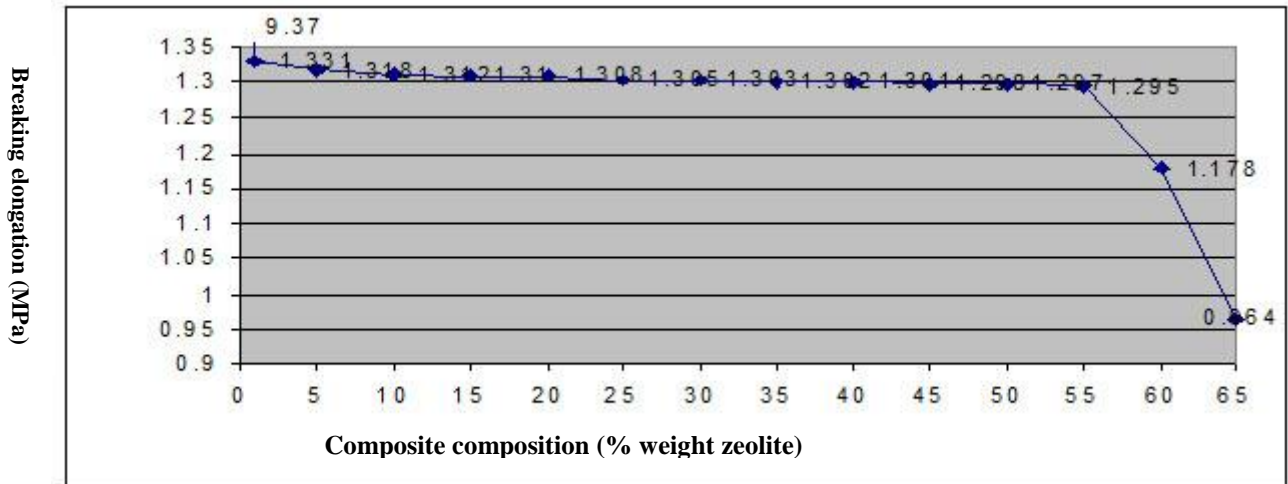


Figure 8 – Composite composition in relation with hardness (Vickers)

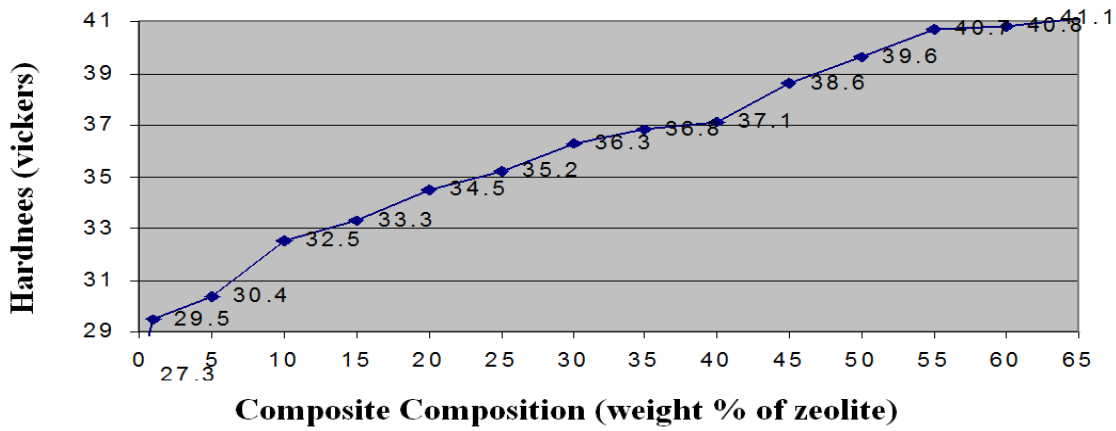
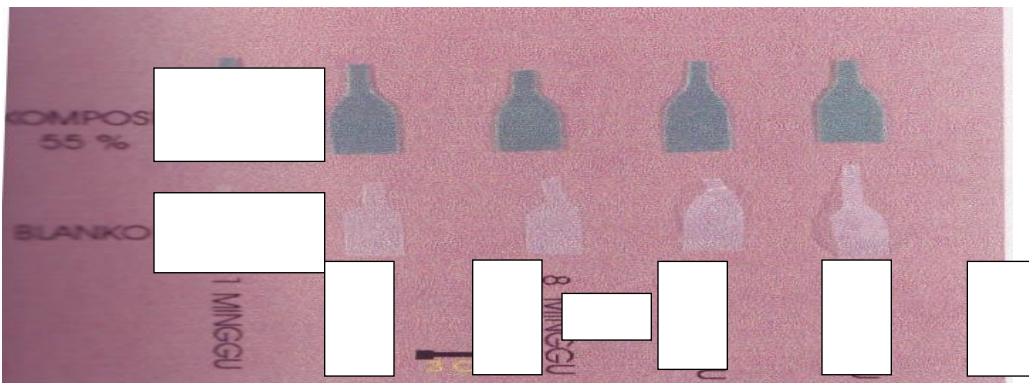


Figure 9 – Sixteen weeks weather test



Tables

Table 1 The degree of crystallinity (X Ray Diffractogram)

Curve	Mass (g)
Total Curve	0,175
Crystallinity Curve	0,093

(Leslie, 2006)

$$X_c = \frac{0.093}{0.175} \times 100\% = 53.14\%$$

Table 2 The density of zeolite - LPDE (%weight) composite

% Zeolite composition	inZeolite (g)	LDPE (g) Zeolite density		LDPE density		Composite density	
			r (Mgm-3)		r (Mgm-3)		r (Mgm-3)
1	0,5	49,5	2,49	0,91		0,91	
5	2,5	47,5	2,49	0,91		0,93	
10	5	45	2,49	0,91		0,95	
15	7,5	42,5	2,49	0,91		1,01	
20	10	40	2,49	0,91		1,03	
25	12,5	37,5	2,49	0,91		1,07	
30	15	35	2,49	0,91		1,13	
35	17,5	32,5	2,49	0,91		1,17	
40	20	30	2,49	0,91		1,21	
45	22,5	27,5	2,49	0,91		1,25	
50	25	25	2,49	0,91		1,33	
55	27,5	22,5	2,49	0,91		1,41	
60	30	20	2,49	0,91		1,46	
65	32,5	17,5	2,49	0,91		1,58	

Table 3 Strength analysis

Composite composition (% weight)	Specimen wide (m ²)	Strength (MPa)	at breakTensile (MPa)	strengthBreaking (MPa)	elongation
0%	0,596	16,756	28,119	9,370	
1%	0,789	16,877	21,223	1,331	
5%	0,790	16,908	21,394	1,318	
10%	0,785	17,008	21,584	1,312	
15%	0,793	17,534	22,167	1,311	
20%	0,788	17,883	22,781	1,308	
25%	0,786	17,997	22,960	1,305	
30%	0,787	18,225	23,158	1,303	
35%	0,791	19,111	24,189	1,302	
40%	0,801	19,902	24,963	1,301	
45%	0,802	20,013	24,983	1,298	
50%	0,792	20,019	25,341	1,297	
55%	0,801	21,123	26,367	1,295	
60%	0,802	18,202	22,695	1,178	
65%	0,790	17,985	22,471	0,964	

Table 4 Vickers Hardness of the composite

Composites composition (%)	Vickers hardness (Hv)
1	29,5
5	30,4
10	32,5
15	33,3
20	34,5
25	35,2
30	36,3
35	36,8
40	37,1
45	38,6
50	39,6
55	40,7
60	40,8
65	41,1