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Addition of Aceh bentonite in an effort to improve the heat resistance properties of polyurethane-based paint coatings

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Abstract

Polyurethane is a polymer compound whose main chain constituent is urethane group (-NHCOO-). Polyurethanes can be mixed with other polymers or other fillers in an effort to enhance and improve the properties of the single polymer. In the need for metal materials that have properties resistant to heat thermal condition and corrosion that can damage the structure, metal coating materials are needed. The priority and novelty of this research is to utilize the natural bentonite which is very potential in the local area to fill polyurethane-based coating paint in order to improve its properties. This research will look at the effect of mixing Polyurethane with Bentonite filler obtained from Nisam, North Aceh which has been modified with CTAB and AgNO3 surfactants. The sample formulation used is polyurethane and polyurethane with North Aceh Bentonite variations of 1.5, 2.5, and 3.5%. Characterization with the addition of Bentonite produces polymers that have good thermal stability capabilities. The addition of Bentonite filler into polyurethane polymer can affect the mechanical properties of the material. The Polyurethane/ Bentonite composite sample has better thermal resistance, where in pure Polyurethane, the initial weight reduction of the pure Polyurethane sample is 50-150℃, the decomposition of pure Polyurethane is at 385℃. For Polyurethane/ Bentonite 98.5:1.5% w/w nanocomposite, the initial weight reduction is 150-300℃, decomposition at 416℃. For Polyurethane/Bentonite 97.5:2.5 w/w, the initial weight reduction is 150-250℃ and decomposition at 430℃. Polyurethane/ Bentonite 96.5:3.5 w/w initial weight reduction is also at 200-300℃ and decomposition at 458℃.

Keywords: Polyurethane, bentonite, surfactant, thermal

1 Introduction

Polyurethane is one of the most popular materials where polyurethane is a synthetic polymer that is widely used in various industries [1]. Polyurethane is an important division of synthetic polymers that are widely used in biomedical applications and various industries. Products containing polyurethane include furniture coatings, construction materials and paints [2].

Polyurethane is a polymer compound whose main chain constituent is a urethane group (-NHCOO-) [2,3]. To synthesize urethane groups can be done by various methods but the most appropriate is the reaction between isocyanate and alcohol. Polyurethanes are different from most other plastic materials, this is because the polyurethane synthesis process allows to control the properties of the final product. Polyurethanes have coating system stability and low thermal barrier properties [4]. To improve the physical properties of polyurethanes (thermal and stracth resistance). Polyurethane can be improved its properties by the addition of Aceh bentonite [5].

Bentonite has received great attention in the paint industry. Bentonite is a trade term for clay containing monmorillonite [5,6]. The main content of bentonite is the mineral montmorillonite (80%) with the chemical formula (Al2O3.4SiO2.X H2O) Based on previous research in the field of polyurethane nanocomposites, it was found that to improve the heat resistance of polyurethane materials, bentonite was added to the polyurethane coating [7]. Bentonite-coated silicates play an important role in providing barrier and heat resistance properties for coating systems [8,9]. Bentonite is a mineral consisting of hydrated alumino-silicate crystals containing alkali or alkaline earth cations in a three-dimensional framework. Bentonite has the ability to expand, ion exchange properties, a large surface area and easily absorbs water, allowing its use as an adsorbent [10-14]

In this study, variations between Aceh Bentonite 1.5, 2.5, 3.5% will be used, then the mixing process will be carried out with Polyurethane. Where with the addition of bentonite can produce paint coatings that have better physical properties and heat resistance. The addition of bentonite to polyurethane will affect the mechanical properties, thermal properties, and morphological structure that can be seen based on SEM tests, FTIR tests, and TGA tests.

2 Materials and Methods

2.1 Material

The materials used in this research are polyurethane, bentonite used from the North Aceh region, Nisam. With other additives Cetyl Trimetyl Ammonium Bromide/ CTAB and AgNO3.

2.2 Methodology

2.2.1 Purification and Opening of Bentonite Interlayer

Weighed as much as 20 grams of bentonite and then ground using a crusher. Filtering was carried out using a 300 mesh sieve shaker. This size can optimize mixing into the polyurethane matrix to form a good crosslink bond (Bala dkk, 2018). A total of 18.2 grams of cetyl trimethyl ammonim bromide (CTAB) was dissolved with 250 mL of distilled water, the solution was heated at 80 ℃ for 1 hour. A total of 20 grams of bentonite was dissolved with 250 mL of distilled water. The bentonite dispersion solution was included in the CTAB solution and stirred for 1 hour. Bentonite was filtered and washed with distilled water several times until there was no more bromide. The filtrate was tested by testing AgNO3 1 M until a white precipitate formed. Bentonite was put into an oven at 60℃ to dry [13].

2.3 Sample Preparation

Prepared 3 containers for polyurethane and bentonite mixture samples. Mixed Polyurethane and Bentonite Aceh (total weight = 20g) with the following ratio: 19,7 g : 0.3 g (1.5% wt); 19.5 g : 0.5 g (2.5% wt); 19.3 g : 0,7 g (3,5%). Polyurethane and bentonite were mixed into a beaker glass and stirred using a magnetic stirrer at 200 rpm for 1 hour. The resulting paint coating was cooled at room temperature and then analyzed for heat resistance using thermogravimetric analysis (TGA).

2.4 Charaterization technique

2.4.1 X-Ray Diffraction Analysis (XRD)

X-ray diffraction (XRD) analysis of the samples was performed using a Shimadzu XRD- 7000 X-Ray Diffractometer Maxima with

a CU anode tube.XRD analysis was used to determine the crystalline form of the material bentonite in Poliurethane matrix.

2.4.2 Analysis of functional groups with Fourier Transform Infra Red (FTIR)

FTIR is used to analyze the characterization of polymeric materials and analyze functional groups present in pure polyurethane and after being combined with fillers. Then it will be seen whether there is a new functional group formed or not. The sample will be crushed with KBr using Shimadzu FTIR spectrophotometer.

2.4.3 Analysis of thermal properties by *thermogravimetric analysis* (TGA)

In principle, this method measures the mass loss of a material when it is heated from room temperature to a high temperature of around 900°C at a rate of heating 20°C [15-17]. This analysis is used as the main analysis to see how much resistance each sample has to the given hot conditions as a benchmark for improving the properties of the material and its fillers.

3 Result and Discussion

3.1 XRD Test Results

The results of X-Ray Diffraction (XRD) characterization of samples can be seen in Figure 3.1.2 The identification results show that pure Polyurethane having a peak at 2Θ= 2.35°. According to Bragg's law, this peak corresponds to a distance of -d 18.5 Å.

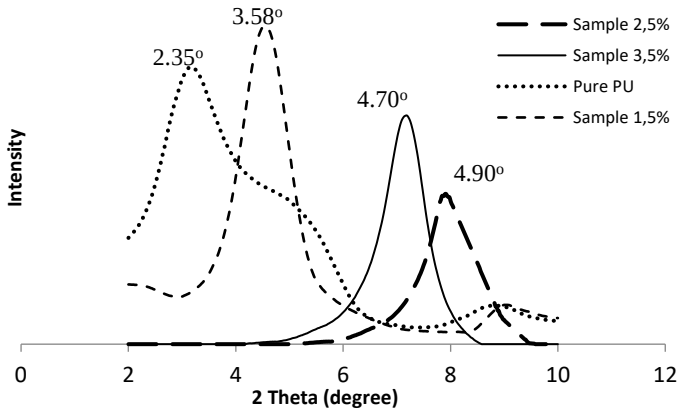

Fig. 1 Result of XRD Analysis

Fig. 1 shown the nanocomposite specimens containing 1.5 and 2.5 wt% did not show any peak in the curve indicating too much distance between the layers. Based on Bragg's law, the initial harmonic peak is in the range 4.70° where the two harmonic peaks should be in the same position in the range of 4.90°. But for this case both are still in the range of PU peak positions. In the 3.5 wt% bentonite nanocomposite sample, a peaks were formed at 2Θ=3.58° [18].

3.2 FTIR Test Results

Preparation of polyurethane coating material shows the results of FTIR analysis showed the formation of N-H urethane groups in polyurethane compounds as evidenced by the absorption of N-H wave numbers that widened at 3310 cm-1 and 3320 cm-1. While the wave number absorption of C=O urethane groups widened at 1729-1734 cm-1, and C-H groups at 2927 cm-1 absorption.

Fig. 2. showed that the functional groups of pure Polyurethane, Polyurethane / Bentonite does not undergo changes in functional groups. Mixing of polyurethane and bentonite does not affect the wavelength absorption of the functional group of polyurethane itself. this is due to the mixing process that takes place only physically bonded without chemical bonding. So that the absence of changes in chemical bonds that occur causes the wavelength absorption of the functional group of Polyurethane / Bentonite detected does not change [19].

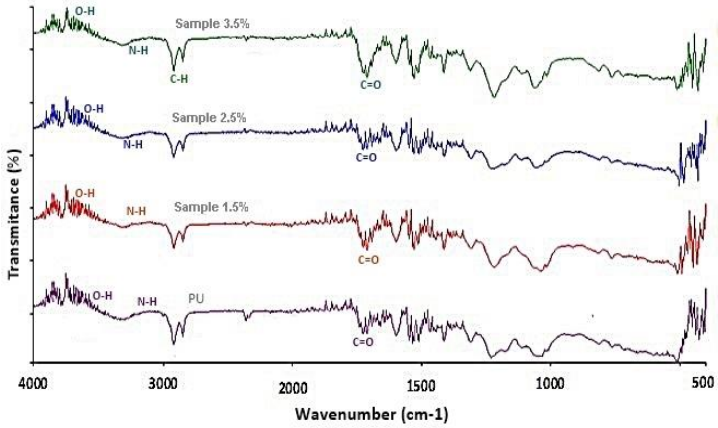

Fig. 2. Result of FTIR Analysis

3.3 Thermal Resistance Testing Results

TGA can be used to characterize any material that shows the change in weight of the material upon heating, and to detect phase changes due to the decomposition process. The process of mass loss in thermal tests occurs due to the decomposition process. The results of thermogravimetric analysis (TGA) of pure Polyurethane and Polyurethane / Bentonite are shown in Table. 1.

Table. 1. Result of TGA Analysis

Sample	Onset Temperature (°C)	Endset Temperature (°C)
Pure PU	50 °C	385°C
1,5 %	150 °C	416°C
2,5 %	150 °C	430°C
3,5 %	200 °C	458°C

Based on the principle of TGA analysis of material thermal stability, the sample with the highest degradation temperature (onset point) and degraded temperature (end point) is the sample with the best thermal stability [20]. Initial weight reduction of Polyurethane pure sample at 50-150 °C, decomposition of Polyurethane pure at 385 °C. For Polyurethane/Bentonite 98.5:1.5% w/w nanocomposite, the initial weight reduction is 150-300 °C, decomposition at 416 °C. For Polyurethane/Bentonite 97.5:2.5 w/w, the initial weight reduction is 150-250°C and decomposition at 430 °C. Polyurethane/Bentonite 96.5:3.5 w/w initial weight reduction is also at 200-300 °C and decomposition at 458 °C. This proves that the addition of bentonite has increased the thermal stability. The increase in degradation temperature is due to the bonding of polymer and filler which melts stronger so that the decomposition of the material becomes slower and harder to break. As previously reported by [21], using bentonite as a supporting material for palm oil-based polyurethane provides better thermal stability marked by an increase in degradation temperature. Good thermal stability will make the material more durable in use in the long term and resistant to high temperature attack in heat energy storage applications.

4 Conclusion

From the results of XRD analysis found containing montmorillonite crystal of the bentonite at peak of 4.9°. The results of FTIR analysis showed that the addition of bentonite to polyurethane doesn't affect the wavelength absorption of the functional groups of polyurethane itself. Based on the thermal test, it was found that the polyurethane layer with the addition of North Aceh bentonite of 3.5% experienced decomposition at the highest temperature of 458°C. It can be concluded that the addition of bentonite can increase the heat resistance of polyurethane which will be applied as a coating paint.

Bentonite which is prepared using surfactants becomes organophilic which is applied as a polymer matrix to optimally increase heat stability.

References

[1] Agusnar, H., Reflianto, D., & Gea, S, "The Manufacture of Palm Oil-Based Polyurethane Nanocomposite with Organic Montmorillonite Nanoparticle as Paint Coatings," *International Journal of ChemTech Research CODEN*, Vol. 7, No.5, 2014.

[2] Ajay, V, R., Krishnan, K., Sabu, T, Polyurethane Polimer, "Application of Polyurethane Based Composite and Nanocomposite", *Polyurethane Polymers*, 559-573, 2017.

[3] Arifullah, M., & Widyastuti, I, Laju korosi baja karbon hasil powder coating dan pengecatan cair," *Jurnal Unmer*, Vol.2, 27-34, 2015.

[4] Arunima, R., Sabu, T, "Polyurethanes: Structure, Propperties, Synthesis, Characterization, and Applications," *Polyurethane Polimer*, Vol.1, 1-16, 2020.

[5] Bala, E, S., Onur, G., Fahri, E., Mahmed, S, C. Contribution of Cations and Layer Changes in the Smectite Structure on Zeta Potential of Ca-Bentonites," *Applied Clay Science*, Vol.143, 415-421, 2019.

[6] Daimei, C., Jian, C., Xinlong, L., Haipeng, J., Zhiguo, X, "Characterization of Anion-Cationic Surfactants Modified Montmorillonite and its Application for Removal of Methyl Orange," *Chemical Engineering Journal*, Vol.171, 1150-1158, 2021.

[7] Gaofeng, W., Shan, W., Zhiming, S., Shuilin, Z., Yunfei, X, "Structures of Nonionic Surfactant Modified Montmorillonites and Their Enchanced Adsorption Capacity Towards a Cationic Organic Dye," Vol. 148, 1-10, 2020.

[8] Gregory, C., Liudmila, N., Sabine, P, " How Efficiently Combine Sonochemistry and Clay Science," *Applied Clay Science*, Vol.119, 193-201, 2020.

[9] Loganathan, S., Valapa, R. B., Mishra, R. K., Pugazhenthi, G., & Thomas, S. "Thermal and Rheological Measurement Techniques for Nanomaterials Characterization," *Micro and Nano Technologies*, Vol. 3, 67–108, 2017.

[10] T Rihayat, S Riskina, Nurhanifa, R Syahyadi, "Effect of Addition of Chitosan-ZnO as an Antibacterial on The Thermal Stability of PLA-Based Nanocomposites for Biofilm Packaging", IOP Conf. Series: Materials Science and Engineering , 854, 012047, 2020

[11] T Rihayat, S Riskina, JP Sirega, J Jaafar, T Cionita, "Making Polyurethanes from castor oil with addition of Bentonite and Chitosan as coating paints on eco-friendly medical device applications", IOP Conf. Series: Materials Science and Engineering, 788, 012046, 2020

[12] M. Borowicz, J. Paciorek-Sadowska, M. Isbrandt, "Synthesis and application of new bio-polyols based on mustard oil for the production of selected polyurethane materials," *Ind. Crop. Prod*, 155, 112831, 2020.

[13] Nakkabi, A., Sadiki, M., Fahim, M., Ittobane, N., Ibnsouda Koraichi, S., Barkai, H., El abed, S., "Biodegradation of Poly(ester urethane)s by Bacillus subtilis," *Int. J. Environ. Res*., Vol. 9, No.1, 2015.

[14] Odetoye T.E., D. S. Ogunniyi., G.A.Olatunji., "Improving Jatropha Curacas Linnaeus Oil Alkyd Drying Properties," *Progress in Organic Coating*, Vol.73, 374-381, 2012.

[15] Paraskar, P. M., Prabhudesai, M. S., Hatkar, V. M., & Kulkarni, R. D, "Vegetable oil based polyurethane coatings – A sustainable approach: A review," *Progress in Organic Coatings*, Vol. 156, 2021.

[16] Q. Mo, W. Li, H. Yang, F. Gu, R. Yang, "Water resistance and corrosion protection properties of waterborne polyurethane coating enhanced by montmorillonite modified with Ce3," *Prog. Org. Coat*, Vol. 136, 105213, 2019.

[17] Teuku Rihayat, Nurhanifa Aidy, Aida Safitri, Atiqah Aida, "Synthesis of poly lactic acid (PLA)/nanochitosan–based for bioscaffold materials with the addition of Zn-curcumin", Materials Today: Proceedings, 63, S526–S531, 2022

[18] Ridwan, Basuki Wirjosentono,Tamrin, R Siburian, Teuku Rihayat, Nurhanifa, "Modification of PLA/PCL/Aceh's bentonite nanocomposites as biomedical materials", AIP Conference Proceedings, 2049, 020008, 2018

[19] S.Y. Li, Z.Y. Liu, L.J. Hou, Y. Chen, T.H. Xu, "Effect of polyether/polyester polyol ratio on properties of waterborne two-component polyurethane coatings," *Prog. Org. Coat*, Vol.141, 105545, 2020.

[20] Wang, X., Cui, Y., Wang, Y., Ban, T., Zhang, Y., Zhang, J., & Zhu, X, "Preparation and characteristics of crosslinked fluorinated acrylate modified waterborne polyurethane for metal protection coating," *Progress in Organic Coatings*, Vol. *158*, 2021.

[21] Nurhanifa Aidy, Rozanna Dewi, Azhari Azhari, Rima Dhinta Dewi Astuti, Teuku Rihayat, "Synthesis of Phase Change Materials Based on Parafin/Graphite with HDPE/PLA as Matrix", Biointerface Research in Applied Chemistry, 13, 5, 425, 2023