# Infrared Spectra and Mechanical Properties of Corn Oil-based Polyurethane Reinforced with Silica Nanoparticles from Rice Husk Ash

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***Abstract*—The incorporation of nanosilica ($SiO_2$) derived from rice husk ash on corn oil-based polyurethane (PU) and the effect of NCO/OH ratio as well as the silica loading were investigated. PU synthesis was carried out via polyaddition reaction between the activated polyol from corn oil and hexamethylene diisocyanate (HMDI). For the PU/$SiO_2$ fabrication, the nanosilica was incorporated before the completion of the PU synthesis. Infrared spectral analyses showed the presence of characteristic bands for PU and $SiO_2$. The mechanical properties of the composite material were strengthened with increasing NCO/OH up to 2:1 ratio and $SiO_2$ content at 5% loading.**

***Index Terms*— Corn oil, polyurethane, rice husk ash, silica nanoparticles**

## I. INTRODUCTION

POLYURETHANE is a broad class of polymer which is known for its versatility in terms of properties and applications [1]. Polyurethane demonstrates excellent tensile strength, high wear resistance and resilience, high flexibility even at low temperatures and is capable of enduring harsh environment conditions [2]. In terms of its usage, PU is being utilized in various applications including but not limited to construction and automotive materials, furniture, coating and biomaterials.

To further extend the applicability of PU, several studies are being done to improve its performance and one of which is the incorporation of fillers. By doing so, remarkable enhancements in mechanical, dielectric, magnetic, thermal, optical, and acoustic properties can be achieved due to the improved filler-polymer matrix interaction [3].

The $SiO_2$ particles have been widely used as nanofillers into polymers to improve their physicochemical properties such as electrical, heat resistance, radiation, and mechanical properties [4]. One possible source of silica is rice husks ash which can be locally obtained and is very easy to procure at a very low price.

The synthesis of polyurethane from the polyaddition reaction between corn oil-based polyol and diisocyanate was earlier reported [5]. In this study, the reinforcement of silica nanoparticles derived from rice husk ash to the polyurethane derived from corn oil was investigated. The infrared spectra and mechanical properties of the composite material was studied with varying NCO/OH ratio and silica loading.

## II. EXPERIMENTAL

The extraction of silica nanoparticles from rich husk ash involved the incineration of the starting material for three hours at 900$^o$C to yield rice husk ashes (RHA). A solution of 1.5L of 1M NaOH and 250g of RHA were mixed then boiled for an hour with constant stirring. The resulting mixture was filtered then the filtrate was collected and cooled to room temp. Afterwards, a 2M HCl was added dropwise into the sodium silicate solution (filtrate) until pH 7.0 before incubation for 10 hours. The resulting silica gel was crushed, washed with distilled water, then was centrifuged. After three washings, the gels were oven dried at 80°C for 24 hours. The extracted silica was then ground until uniform powder size was achieved [6].

For the synthesis of the polyurethane, a calculated amount of 0.05 mol of corn oil in a three-necked round bottom flask was heated to 90°C with constant stirring. Then, a corresponding amount of 1.5 mol 30% $H_2O_2$ in a 60mL solution with water was added dropwise followed by the addition of 0.3 mol formic acid in a 60mL solution with water. The reaction temperature was maintained at 90°C for 6 hours, after which, the less dense epoxidized oil was collected. After epoxidation, the oil was heated to 64°C in the same set-up followed by the addition of stoichiometric amounts of distilled water, formic acid, and methanol. This epoxide ring opening procedure was held for 30 minutes. The mixture was left to cool and settle for the collection of the denser organic polyol [5,7].

The activated corn oil-based polyol was reacted with hexamethylene diisocyanate (HDI) to synthesize PU with the following NCO/OH ratios: 1:1, 2:1, and 3:1. The total volume of PU and PU/$SiO_2$ was kept at 6.5mL, and the

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reaction was carried out at 90°C for 3.5 hours with constant stirring. Varying amounts of silica, 5 and 10 wt%, was added an hour before the completion of the PU synthesis reaction. The synthesized PU and PU/$SiO_2$ were casted and cured at room temperature followed by oven curing.

The extracted silica from rice husk ash was characterized under Fourier Transform Infrared Spectroscopy (FTIR) in order to verify the presence of silica and Brunauer-Emmett-Teller (BET) test for the particle size. The synthesized PU and PU/$SiO_2$ materials were analyzed via Fourier Transform Infrared Spectroscopy (FTIR) for the compositional analyses and Universal Testing Machine (UTM) for the mechanical properties.

## III. RESULTS AND DISCUSSIONS

The infrared spectral analysis of the nanosilica extracted from the RHA is shown in Figure 1. The peak at 800 $cm^{-1}$ denotes the Si-O-Si stretch backbone of the nanosilica particles. The O–H and Si-O vibration absorptions were ascribed at around 3300 $cm^{-1}$ and 1100 $cm^{-1}$ respectively and these two bands correspond to the silanol groups [7-9]. The peak found at around 1600 $cm^{-1}$ is attributed to the bending vibration absorption of physically adsorbed water [7]. The average particle size determined through BET test is around 410 Å.

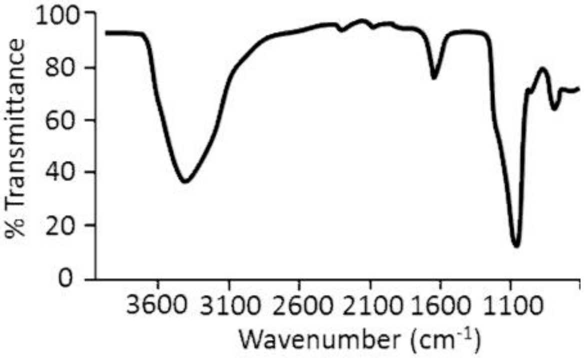

Fig. 1. Infrared spectrum of nanosilica derived from RHA

The infrared spectra of pristine corn oil-based PU are shown in Figure 2. The characteristic peak at 2900 $cm^{-1}$ is within the C-H stretch region and at around 3400 $cm^{-1}$ corresponds to a secondary amine group. Various peaks include C=O (around 1700 $cm^{-1}$), C-H (around 1400 $cm^{-1}$) and N-H (around 1500 $cm^{-1}$), as well as C-N (around 1200 $cm^{-1}$) and C-O-C (1000 $cm^{-1}$) bonds. The presence of N-H and C=O corresponds to the amide groups present in polyurethane [10-11]. Comparing the spectra of the synthesized PU at different NCO/OH ratio, the peak of the N-H bond at 3400 $cm^{-1}$ is more distinct in the sample with 2:1 NCO/OH. Otherwise, there is no significant difference in terms of the spectral behavior of the synthesized PU at different NCO/OH ratio.

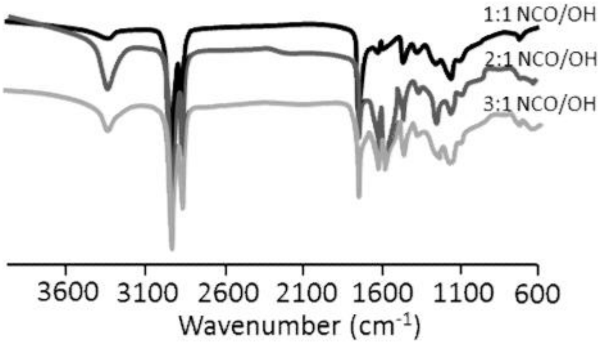

Fig. 2. Infrared spectra of pristine PU at different NCO/OH ratio

Representative infrared spectra of the PU/$SiO_2$ composite with 2:1 NCO/OH ratio are shown in Figure 3. The bonds within 900 $cm^{-1}$ to 1300 $cm^{-1}$ were amplified with increasing amount of silica which is attributed to the Si-O bond absorption. The peak at around 3200 $cm^{-1}$ to 3500 $cm^{-1}$ diminishes as silica content increases.

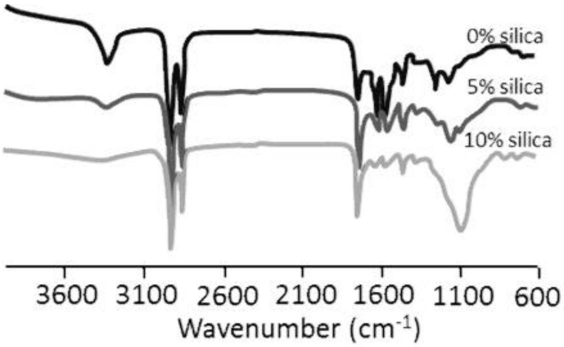

Fig. 3. Infrared spectra of PU/$SiO_2$ with 2:1 NCO/OH ratio at different silica loading

The mechanism involves in the incorporation of silica into the PU structure is given in the schematic reaction as shown in Figure 4. The extracted silica nanoparticles were surrounded by silanol (-OH) groups. Considering the rapid reaction between –NCO and –OH groups, these silanol groups can react with the terminal –NCO groups of the formed PU pre-polymer. The reaction between these two groups binds the PU pre-polymer to the $SiO_2$ particle, thus aiding to the increase in crosslink density of the growing polymer structure as well as the viscosity of the PU/$SiO_2$ mixture [12].

The stress-strain diagram of the synthesized PU/$SiO_2$ at 5% loading is shown in Figure 4. The modulus and ultimate tensile stress were found to increase with increasing NCO/OH ratio, while the elongation at break decreases with increasing NCO/OH ratio. This observation shows that the PU/$SiO_2$ material is strengthened with increasing NCO/OH

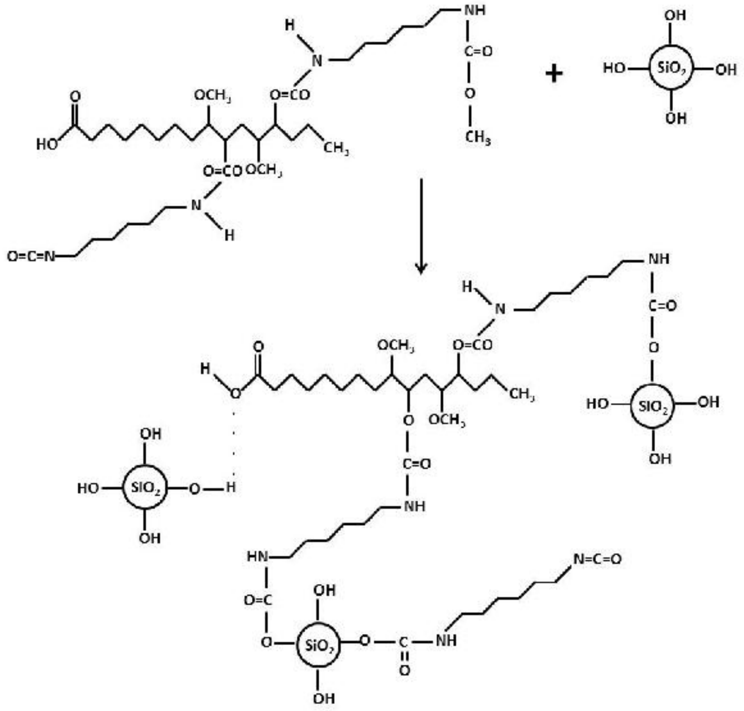

Fig. 4. Proposed polymer reaction mechanism of PU/$SiO_2$ interaction

ratio. This strengthening is associated with the increase in crosslinking density of the hard segment of the material. However, the increase in rigidity compromises the materials ductility as reflected by the decrease in the material's maximum elongation.

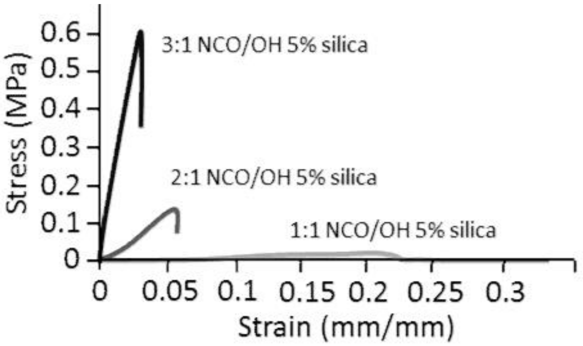

Fig. 4. Stress-strain plot of PU/$SiO_2$ with 5% loading at varying NCO/OH ratio

The effect of silica content on the modulus, ultimate tensile stress and maximum elongation of the PU/$SiO_2$ materials was illustrated in Figures 5, 6 and 7 respectively. The 10% silica loading can cause the decrease of the mechanical properties of the composite material. Higher loading of filler can lessen the interaction of the polymer-nanosilica system. Considering the polyurethane samples with 3:1 NCO/OH ratio at 5 wt% silica, the modulus and ultimate tensile stress of the PU and PU/$SiO_2$ materials increases with increasing silica content. Moreover, the maximum elongation is inversely proportional with the silica content. This could be associated with increasing attraction between silica particles which could cause a decrease in silica–PU matrix adhesion.

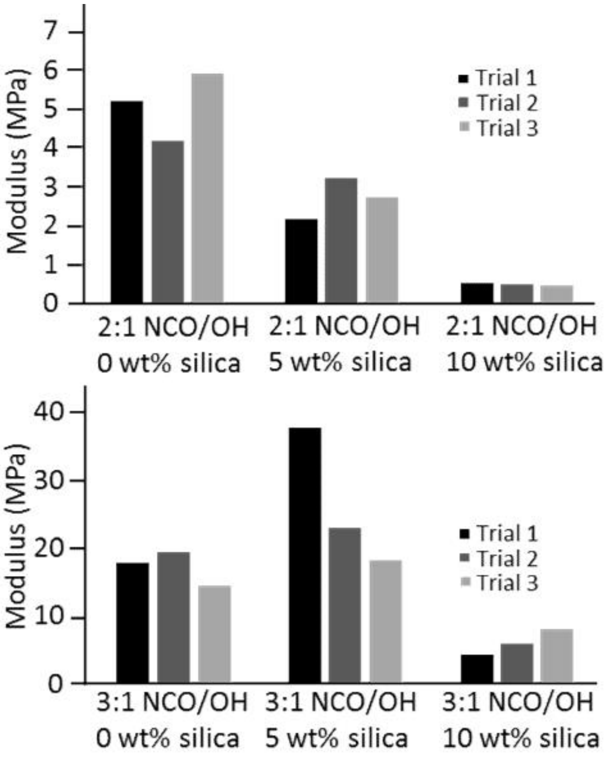

Fig. 5. Modulus of PU and PU/$SiO_2$ with varying NCO/OH ratio and silica loading

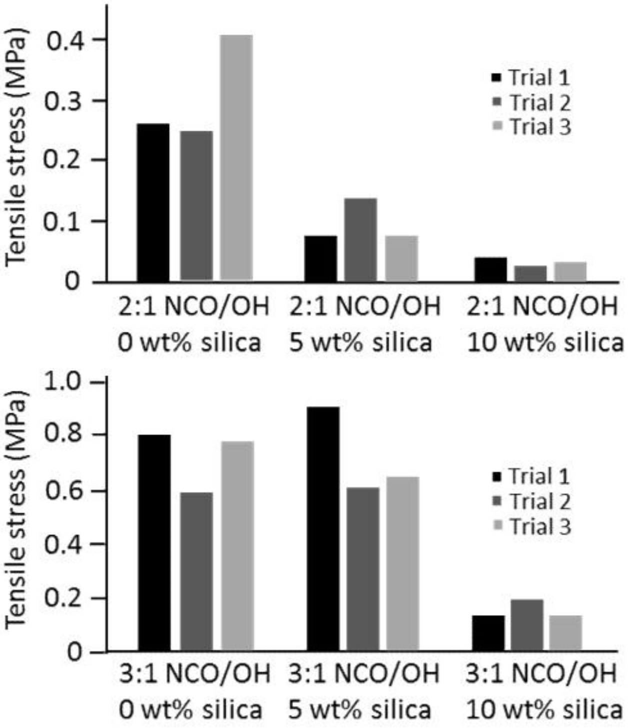

Fig. 6. Tensile strength of PU and PU/$SiO_2$ with varying NCO/OH ratio and silica loading

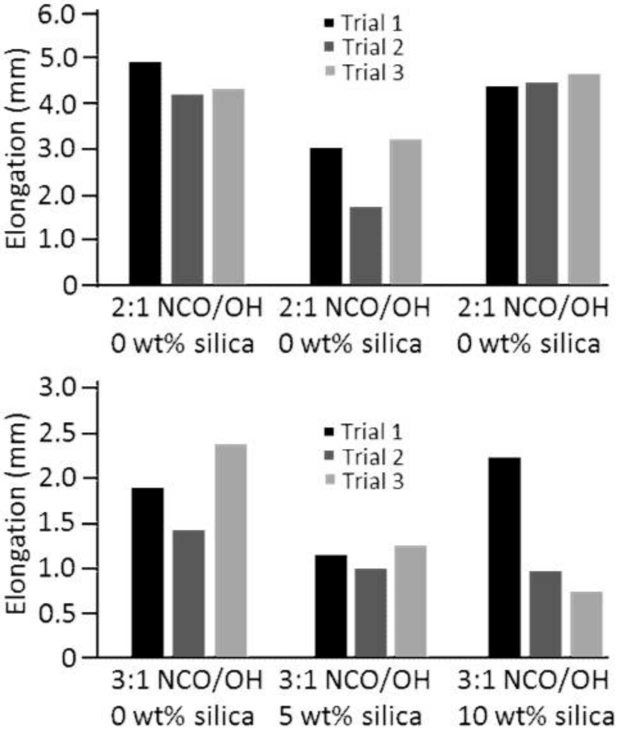

Fig. 7. Elongation of PU and PU/$SiO_2$ with varying NCO/OH ratio and silica loading

Higher NCO/OH ratio can lead to higher mechanical properties of the material. The silanol groups of silica particles react with terminal isocyanate groups of PU. Thus, at higher NCO/OH ratio, more silanol–isocyanate bond could be formed, which increases the silica–PU matrix adhesion. Furthermore, with more of these bonds present, the effect of silica as reinforcing material is well demonstrated.

## IV. CONCLUSION

The nanosilica derived from rice husk ash was successfully incorporated in the corn oil-based polyurethane materials. The effect of the NCO/OH ratio and the amount of silica reinforcement on the fabricated PU and PU/SiO2were determined. With the increasing NCO/OH ratio, the PU and PU/$SiO_2$ were strengthened but with compromised ductility.

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The mechanical properties such as hardness, tensile strength, and modulus of polyurethane can be dictated by the increase of NCO/OH ratio. However, the maximum ratio with desirable properties is only up to 2.4. Further increase in the content of the hard segment in the polyurethane can now cause a decrease in the mechanical properties [13].

## REFERENCES

[1] P. Cinelli, I. Anguillesi and A. Lazzeri, “Green synthesis of flexible polyurethane foams from liquefied lignin”, *European Polymer Journal*, vol. 49, pp. 1174-1184, 2013.

[2] J. Zhang, T. Weiping and D. Zilin. “Synthesis and characterization of transparent and high impact resistance polyurethane coatings based on polyester polyols and isocyanate trimmers”, *Progress in Organic Coatings*, vol. 75, pp. 579-583, 2012.

[3] X. Gao, Z. Yanchao, X. Zhao, Z. Wang, D.An, Y. Ma, S.Guan, Y. Du and B. Zhou, "Synthesis and characterization of polyurethane/$SiO_2$ nanocomposites", *Applied Surface Science,* vol. 257, pp. 4719-4724, 2011.

[4] J. Lin, X. Wu, C. Zheng, P. Zhang, B. Huang, N. Guo and L. Jin, “Synthesis and properties of epoxy-polyurethane/silica nanocomposites by a novel sol method and in-situ solution polymerization route”, *Applied Surface Science*, vol. 303, pp.67-75, 2014.

[5] F. L. Fajardo, J.R. dela Pena, J. Bayani and E.Magdaluyo, Jr., "Preparation and characterization of polyurethane films using corn (Zea mays L.) oil-based polyol”, *MATEC Web of Conferences* , vol. 43, pp. 1-4, 2016.

[6] U. Kalapathy, A. Proctor and J. Shultz, "An improved method for production of silica from rice hull ash", *Bioresource Technology*, vol. 85, pp. 285-289, 2002.

[7] A. Hazmi, S. Ahmad, M.M. Aung, L.C. Abdullah, M.Z. Salleh and M.H. Mahmood, "Producing jatropha oil-based polyol via epoxidation and ring opening," *Industrial Crops and Products*, vol. 50, pp. 563–567, 2013.

[8] X. Ying-Mei, Q. Ji, H. De-Min, W. Dong-Mei, C. Hui-Ying, G. Jun, and Z. Qiu-Min, “Preparation of amorphous silica from oil shale residue and surface modification by silane coupling agent”, *Oil Shale*, vol. 27, pp. 37-46, 2010.

[9] X. Gao, Y. Zhu, X. Zhao, Z. Wang, D. An, Y. Ma, S. Guan, Y. Du and B. Zhou, "Synthesis and characterization of polyurethane/SiO2 nanocomposites", *Applied Surface Science*, vol. 257, pp. 4719-4724, 2011.

[10] A. Asefnejad, M.T. Khorasani, A. Behnamghader, B. Farsadzadeh and S. Bonakdar, “Manufacturing of biodegradable polyurethane scaffolds based on polycaprolactone using a phase separation method: physical properties and in vitro assay”, *International Journal of Nanomedicine*, vol. 6, pp. 2375-2384.

[11] University of Colorado at Boulder, Department of Chemistry and Biochemistry. “IR Spectroscopy Tutorial: How to analyze IR spectra.” August 31, 2015. Available from: http://orgchem.colorado.edu/Spectroscopy/irtutor/analyzeir.html

[12] L. Chen, X. Wang, Z. Jia, Y. Luo and D. Jia, “Use of precipitated silica with silanol groups as an inorganic chain extender in polyurethane”, *Material and Design*, vol. 87, pp. 324-330.

[13] M. Mohammed, M. AL-Jarrah and A. Abdul Lateef, “Effect of NCO/OH on the Mechanical properties of Polyurethane Elastomers.” *The 1$^{st}$ Regional Conference of Eng. Sci. NUCEJ Spatial*, vol. 3, pp. 485-493.