

August 10, 2005

Dr. Christopher C. Ibeh
PSU/NSF – REU/RET Director
Department of Engineering Technology
Pittsburg State University
Pittsburg, Kansas 66762

RE:

Dear Dr. Ibeh:

It is a privilege to present to you the culmination of my summer research on the AFM analysis of Soy based PU Nanocomposite.

This paper will review the basics of nanocomposites and soy based polyurethane. There is a great potential market for these nanocomposites. The AFM scans of the soy based PU will help us identify relationship between the surface texture percent composition of nanocomposites.

Sincerely,

Austin M. Baldwin

Pc: Student, Physics, Pittsburg State University

AFM analysis of Soybean based PU Nanocomposite.

July 22, 2005

By

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2005 PSU-CNCMM REU/RET

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AFM analysis of Soybean based PU Nanocomposite.

**Austin Baldwin, Senior in Physics,
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1. ABSTRACT

In recent years, new processes have been developed using soybean oil to make plastic. By using the renewable resource of soybean oil instead petrochemicals the production cost will be reduced while still providing a product with similar properties to the version made with petrochemicals. Soybean oil is mixed with an isocyanate to create a polyol which in turn is used to manufacture polyurethane. Soybean oil can also be used as an ingredient in reactive thermoset resins. It is these resins that are being tested for this study. The main purpose of this research is to analyze the surface texture of mechanically reinforced polyurethanes, and study the influence of the concentration of the Nanoclay on the properties of the new material. Two different soybean oil based polyols, SOY169 and SOY201 were selected to synthesize the polyurethane nanocomposites using a diisocyanate (MDI) as a curing agent. The clay used at different concentrations (0%, 1%, 3%, and 5%) in the synthesis of the nanocomposite polyurethane was organo modified Montmorillonite clay, Cloisite®10A. Methanol, was chosen as the solvent media in preparing the samples. Several methods were used to find the properties of the samples. Mechanical tests for Tensile strength, Flexural strength, and Notched Izod Impact strength; Thermal analysis, and Atomic force microscopy (AFM) were used to identify the properties of the materials.

2. Introduction

Nanocomposites are made by adding nano material into a plastic resin to give it added strength and other desired properties. Nano-size materials are favored for many applications due to their large surface area and at least one dimension on a nanometer scale. An increase in available surface area can increase the reactivity of reagents and catalysts. Nanocomposites that contain small amounts of plate-like nanoclay particles, in this case (Cloisite®10A), have improved mechanical and thermal properties compared to the base resins. They also have better barrier performance and flame retardency without increasing the weight or affecting the transparency according to the manufacture. The nanoclay particles are a naturally occurring form of smectite. The trick is getting them to disperse correctly in polymers. This creates favorable conditions for exposure of all its surface area to the polymer. This is referred to as exfoliation with out proper exfoliation the full application of its properties cannot be realized.

Southern Clay is working with General Motors (GM) and Basell to produce nanocomposite that is being introduced on some GM models. The parts are stiffer, lighter, and less brittle at low temperatures than conventional composites made with fillers such as talc. The overall market for nanoclays is small, but in the near future the market has great potential for growth as more applications are commercialized.

When mixing the nano clay in liquid form, lower levels of clay must be used because as the nano clay disperses the viscosity of the fluid increases causing the vortex to decrease. Oils are used for polymer applications because they are relatively nonreactive and help form important parts of the structure. By using soybean oil and isocyanates we can create a renewable polyurethane that can go head to head with those made with fossil fuel. The manufacturers say that the insertion of Nanoparticles in the polymer matrix should increase the modulus of elasticity and perhaps the strength. In this research two different soybean oil based polyols SOY169 and SOY201 were selected to synthesize the polyurethane nanocomposites using a diisocyanate as a curing agent. The polyols had a significant difference in their crosslinking density. The clay used in the synthesis of the nanocomposite polyurethane was a smectite clay additive with flakes that are only one nanometer thick (one-millionth of a millimeter) and 500-2000 nm long. The surface area of this smectite clay is around 700m²/g. The trade name of this clay is Cloisite®10A, which is natural montmorillonite clay modified with a quaternary ammonium salt. The amount of diisocyanate was determined according to the OH number of the polyols. Several testing methods are employed to analyze the samples. Mechanical tests were carried out to estimate the effect of particle concentration on tensile strength and elongation at break, impact resistance and flexural modulus. Equilibrium swelling in toluene was also measured to determine whether the nanoparticles had an effect on crosslinking density (curing of polyurethanes). X-ray diffraction, atomic force microscopy (AFM), and other techniques were used to analyze the structure and morphology of the polymer nanocomposite. Fourier transform infrared spectroscopy (FT-IR) was used to evaluate whether or not new chemical bonds were formed.

3. Literature Review

[1] This article gives a brief history on the AFM and discusses the basic principles on how it operates. The strengths and weaknesses of the AFM in comparison to other scanning microscopes. http://en.wikipedia.org/wiki/Atomic_force_microscope

[2] This article reviews market value potential and possible future uses for a soy based plastic. It also discusses that these renewable resources can compete with their petrochemical counterparts. http://www.unitedsoybean.org/newuses/targets_soybased_plastics.html

[3] This paper discusses the source of natural nanoclay comes from, how it was formed, how much nanoclay there is and how SPC can give us a consistent supply. <http://www.nanoclay.com/>

[4] GM teams up with southern clay Products and others to produce a nanocomposite side step assist for their GMC safari and the Chevrolet Astro van. This is the tip of the iceberg showing the potential for market growth and profit from nanocomposites. <http://www.nanoclay.com/gmrelease.pdf>

[5] This article says it all in the title the amazing thing is that the article was written in 1999 and many of the things hold true today. They found that a small percentage on nano clay filler can increase properties by astounding amounts. This potential of improvement in physical properties allow these nanocomposites to be competitive with costlier engineering resins. The other main issue in this article is the possible market for use in the auto industry. Buy making automobile body panels out of these nanocomposites a automakers can reduce weight and cost while maintaining quality and safety. I one word nanocomposites are the future. June 1999 *Plastics Technology* Nanocomposites: A Little Goes A Long Way

By Lilli Manolis Sherman, Senior Editor

4. Background Information

a. Nanoclay

Nanocomposites are made by adding nano material into a plastic resin to give it added strength and other desired properties. nano-size materials are favored for many applications due to their large surface area and at least one dimension on a nanometer scale . An increase in available surface area can increase the reactivity of reagents and catalysts. Nanocomposites that contain small amounts of plate-like nanoclay particles, in this case (Cloisite®10A), and have improved mechanical and thermal properties compared to the base resins. They also have better barrier performance and flame retardency without increasing the weight or affecting the transparency according to the manufacture. The nanoclay particles are a naturally occurring form of smectite. The clay used in the synthesis of the nanocomposite polyurethane was a smectite clay additive with flakes that are only one nanometer thick (one-millionth of a millimeter) and 500-2000 nm long. The surface area of this semctite clay is around $700\text{m}^2/\text{g}$. The trade name of this clay is Cloisite®10A, which is natural montmorillonite clay modified with a quaternary ammonium salt.

The mixing nano clay in liquid form should be done with lower levels of clay because as the nano clay disperses the viscosity of the fluid increases causing the mixing vortex to decrease. Although with higher viscosity more energy is transferred to the packets of nanoclay causing more platelets to separate from one another in a plastic matrix. During exfoliation platelets at the outermost region of each packet cleave off, exposing more platelets for separation. Oils are used for polymer applications because they are relatively nonreactive and help form important parts of the structure. By using soybean oil and isocyanates we can create a renewable polyurethane that can go head to head with those made with fossil fuel. The manufactures say that the insertion Nanoparticles in the polymer matrix should increase the modulus of elasticity and perhaps the strength. In this research two different soybean oil based polyols SOY169 and SOY201 were selected to synthesize the polyurethane nanocomposites using a diisocyanate as a curing agent. The polyols had a significant difference in their crosslinking density. The clay used in the synthesis of the nanocomposite polyurethane was a smectite clay additive with flakes that are only one nanometer thick (one-millionth of a millimeter) and 500-2000 nm long. The surface area

of this smectite clay is around 700m²/g. The trade name of this clay is Cloisite®10A, which is natural montmorillonite clay modified with a quaternary ammonium salt.

b. Atomic Force Microscope

Along with the many test that were ran on the samples the main focus of this research was the AFM scans. The (AFM) or the Atomic Force Microscope is a device that is used to take topographical pictures of samples at high magnification. Gerd Binnig and Heinrich Rohrer were two men that made great breakthrough in scanning probe microscopes. They found that if one could keep a metal probe about 1.0×10^{-10} meters from the surface of a conductive sample tunneling forces can be detected. From these forces the displacement of the cantilever could be measured. The other big achievement in AFMs was being able to scan non-conductive materials. The probe tip is attached by a cantilever that has a spring constant less than the atomic force that attaches the atoms of the sample. The amount that the tip moves is equivalent to the force that the sample exerts on the tip which is shown by the equation $F_{spring} = -k \cdot \Delta Z$ the spring constant of must be less than $\omega^2 m$.

5. Methodology

5.a Equipment used

1. LG Oscilloscope OS-9020A
2. True Image SPM software
3. Newport Pneumatic Table
4. Burleigh AFM
5. METRIS-3352 PROBES (Nanosensors, Reflective Coating)
Burleigh PN 07345-3-00

5.b Materials used

1. Samples that were used were prepared by Rama Etekallapalli Senior, Plastics Engineering Technology Pittsburg State University. The method used is outlined in Appendix A
2. Acetone
3. Wet 'n' Wild nail polish

5.c Sample Preparation

1. After obtaining a sheet of sample material it was cut to fit the size of the mount.

2. A dab of Wet 'n' Wild nail polish was applied to the mount so that the sample piece would adhere to the mount.

5.d Probe Preparation

1. Put small drop of Wet 'n' Wild nail polish on the etched square of the probe mount. Then take a probe tip with the non magnetic tweezers and place on probe mount in center of the square try to make the tip perpendicular to the probe mount. Then let dry.

5.f Testing procedure

Aligning the detector:

1. Make sure the FEEDBACK ACTIVE indicator is off.
2. If the FEEDBACK ACTIVE indicator is on (METRIS Electronic Controller), reset the electronic controller by momentarily pressing the COARSE RETRACT switch.
3. Select the ACTUAL FORCE AMPLITUDE/CURRENT of the SPM MONITOR on the electronic controller.
4. Select the Detector Alignment option from Calibrate menu in the True Image SPM Software. A target and a cross hair appear on the screen. The target and the cross hair represent the detector and the laser beam, respectively. To align the laser beam on the center of the detector, you must bring the cross hair close to the center of the target by mechanical adjustment. The X and Y detector alignment knobs, located on the left side panel and the rear panel of the head are used for moving the Probe module in X and Y directions.
5. Slowly turn the Y detector alignment knob on the rear panel of the head to bring the cross hair onto the vertical axis of the target. If the cross hair moves up or down instead of in the horizontal direction, continue turning the knob slowly until the cross hair jumps from the left side of the target to right. Continue turning in the same direction until the cross hair is close to the vertical axis of the target.
6. Slowly turn the X detector alignment knob on the left side panel of the head to bring the cross hair close to the center of the target.
7. You may need to alternate between the rear and left detector alignment knobs to bring the cross hair close to the center of target.
8. Make sure you have selected the ACTUAL FORCE/CURRENT of the SPM MONITOR on the front panel of the electronic controller. Monitor the LED display of the SPM MONITOR, while adjusting the detector position. The ACTUAL FORCE AMPLITUDE/CURRENT must be adjusted close to zero (within ± 1.0 volt).
9. Click on the Exit button in the Detector Alignment window to return to the previous screen.

10. If the FEEDBACK ACTIVE indicator on the front panel of the METRIS Electronic Controller is on, momentarily press the COARSE RETRACT to reset the feedback.

Configuration of Non Contact mode:

1. Select Configuration from the Collect menu.
2. Select Non Contact in the Contact Mode box.
3. Use the maximum number of Data points in the X and Y directions (recommend max of 256 samples).
4. Set the Number of substeps to 4 or 8 (16 is not available on all scans).
5. Set the Scan Range (size of area scanned) in X and Y directions.
6. Set the Scan Range Scale to automatic.
7. Set the Sample Delay and Retrace Delay.
8. Set the Scanline Delay.
9. Set the Frame Delay (minimum of 150 mSec is recommended).
10. Select Topographic data type.
11. Turn on Tilt Removal.
12. Turn off the Linearity (unless working with 70 pam scan module above 25 pam scan range).
13. Turn on the Single Scan mode.
14. Click on OK to exit the Configuration menu.

Electronic Controller Setup for Non contact Scanning:

1. Set the SPM MONITOR knob to OSC AMPLITUDE. Use the BIAS VOLTAGE/OSC AMPLITUDE knob to set the reading to ~0.5 volt.
2. Select Non Contact Tuning from the Calibrate menu, and then select Scan from the submenu. From the Scan dialogue box, select Configure.
3. Set the Non Contact Tuning Configuration parameters.
 - Select *Frequency* in the *Horizontal Axis* box.
 - Select the desired *Number of pixels* (256 is recommended)
 - *Initial Frequency* (150 KHz is recommended)
 - *Final Frequency* (200 KHz is recommended)
 - *Minimum Amplitude* (0 V is recommended)
 - *Maximum Amplitude* (35 V is recommended).
 - Set the *Number of scans to average* (2 is recommended).
 - Set the *Sample Delay* (20.00 is recommended)
 - Set the *Frame Delay* (0.00 is recommended).
 - Select *Average Scan Mode*.
 - Click *OK* to return to the *Scan* window.
1. To eliminate any offset in the frequency scan, set the REFERENCE FORCE AMPLITUDE/CURRENT knob to zero.
2. Click on *Scan*.
3. Press [C] to capture a scan.

4. Click Exit
5. Select Non Contact Tuning from the Calibrate menu, and then select Analysis from the submenu.
6. Use the arrow keys on the keyboard to move the vertical cursor to the peak of the waveform.
 - If you do not see a peak, make sure that the REFERENCE FORCE AMPLITUDE/CURRENT knob is set to zero. If the REFERENCE FORCE AMPLITUDE/CURRENT knob is set to zero change the initial and final frequency values in the configuration window (step 3) to bracket the expected resonant frequency of the probe.
7. Note the *Offset* value of the frequency of the peak in the window and click *OK*.
8. Select Non Contact Tuning from the Calibrate menu, and then select Scan from the submenu. From the Scan dialogue box, select Configure.
9. Set the Non Contact Tuning Configuration parameters
 - Set the *Initial Frequency* to about 5 KHz less than the *Offset* value noted in step 7
 - Set the *Final Frequency* to about 5 KHz more than the *Offset* value noted in step 7
 - Leave all other values the same.
10. Set the SPM MONITOR knob to ACTUAL FORCE AMPLITUDE/CURRENT. Then adjust BIAS VOLTAGE/OSC AMPLITUDE until the reading reaches a value between 30 and 35 volts.
11. Click on Scan.
12. If the resonant peak is too small, use the BIAS VOLTAGE/OSC AMPLITUDE knob to increase the amplitude. If the resonant peak is too high, decrease the amplitude
13. Press [C] to capture a scan
14. Click Exit
15. Select Non Contact Tuning from the *Calibrate* menu, and then select *Analysis* from the submenu.
16. Use the arrow keys on the keyboard to move the vertical cursor over the steepest part of the slope just to the left of the peak.
17. Note the *Value* of the frequency of the steepest part of the peak in the window and click *OK*.
18. Set the SPM MONITOR knob to REFERENCE FORCE AMPLITUDE/CURRENT, and use the REFERENCE FORCE AMPLITUDE/CURRENT knob to set the SPM MONITOR readout to about 3/4 of the value noted in step 17
19. Make sure the FEEDBACK ACTIVE indicator is off. If the FEEDBACK ACTIVE indicator is on, press the COARSE RETRACT down to reset the feedback.
20. Set the Proportional Gain to 12 o'clock.
21. Set the Integrator Gain to 3 o'clock.
22. Set the Differentiator Gain to minimum.

23. Set the LowPass Filter to 12 o'clock.
24. Set the X and Y OFFSET scan controls so that their two middle indicator bars are lit. This zeros the X and Y OFFSET.
25. Set the MAGNIFICATION knob to the desired zoom.

Auto Approach:

1. To start the automatic approach, simply toggle the AUTO APPROACH switch up momentarily. The AUTO APPROACH indicator illuminates. The scanning module continues approaching the probe until a force/amplitude equal to the pre-set reference force/amplitude is detected. The automatic approach automatically stops and the feedback activates. At this point, the AUTO APPROACH indicator goes out and the FEEDBACK ACTIVE indicator LED goes on.
2. Monitor the ACTUAL FORCE AMPLITUDE/CURRENT on the controller. The reading should be close to the reference voltage (5 volts, ± 0.5 for contact mode and -15 to -20 volts for non contact mode).
3. If using an oscilloscope monitor the waveform for an AC signal.
4. If the ACTUAL FORCE AMPLITUDE/CURRENT reading is not close to the reference setting or there is no AC signal on the oscilloscope, this indicates a false engagement.
5. Press COARSE RETRACT to reset the electronic controller and turn the FEEDBACK ACTIVE indicator off. Auto approach again.

Acquiring Images:

1. Select *Scan Control* from the *Collect* menu.
2. Select *Scan* in the *Scan Control* window.
3. To optimize the image quality, for the *Topographic* mode during a scan, take the following steps:
 - a. Increase the LOWPASS FILTER to within a range of 12 to 3 o'clock, while monitoring the image or the oscilloscope output of actual force. Make sure you see minimal oscillations on the image. The oscilloscope trace should show minimum AC components.
 - b. Increase the PROPORTIONAL GAIN until the feedback oscillates. Then turn it back slightly. This manifests itself as grainy image or regular oscillatory patterns on the screen which do not scale with the image magnification. A severe oscillation may also be accompanied by high frequency sound resulting from the fast Z motion of the PZT scanner. A proper setting results in an optimal constant value of the oscilloscope trace. However, you will see small "over or under" shoots when scanning over large steps.
 - c. Increase the DIFFERENTIATOR GAIN until the feedback oscillates. Then turn it back slightly. The resulting response should be similar to the results of the optimization with the PROPORTIONAL GAIN. The DIFFERENTIATOR GAIN however allows the feedback to follow

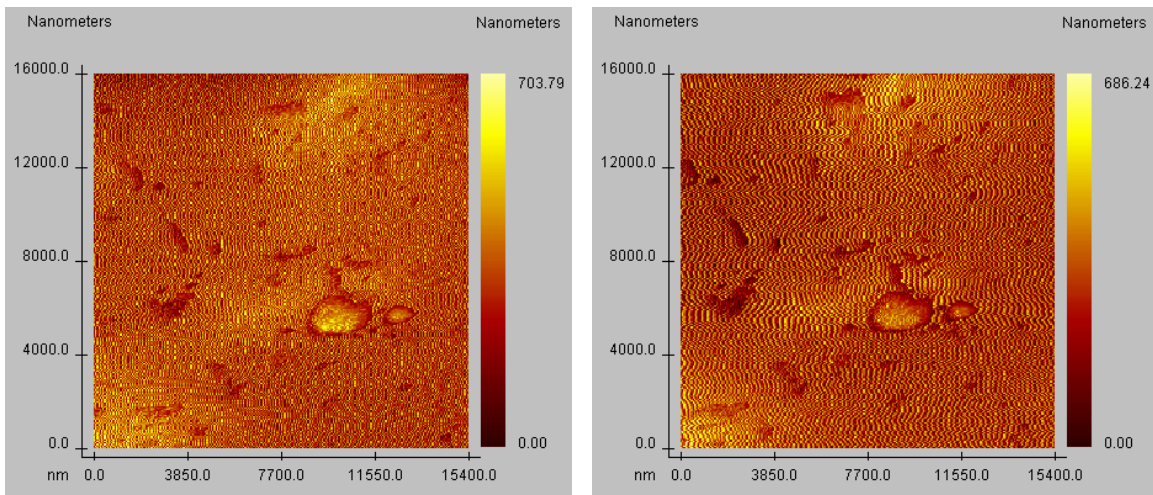
features such as steps. Pay attention to steep edges such as the edges of tall or deep features in your images.

- d. To restart the scan after making the above adjustments, press [H] to halt the scan, then press [Enter].

6. Results and Evidence

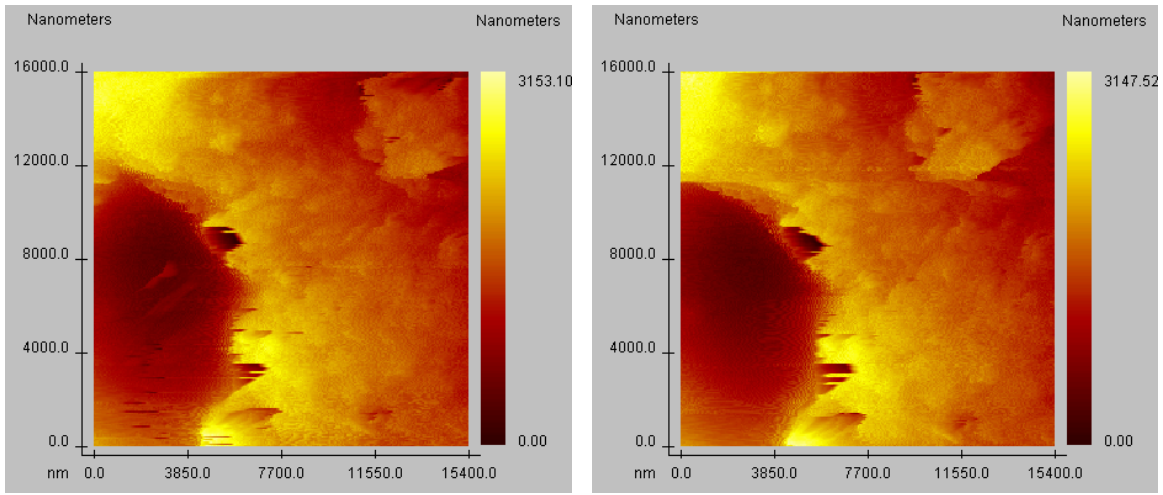
SOY 169 1% REPRODUCIBILITY

A

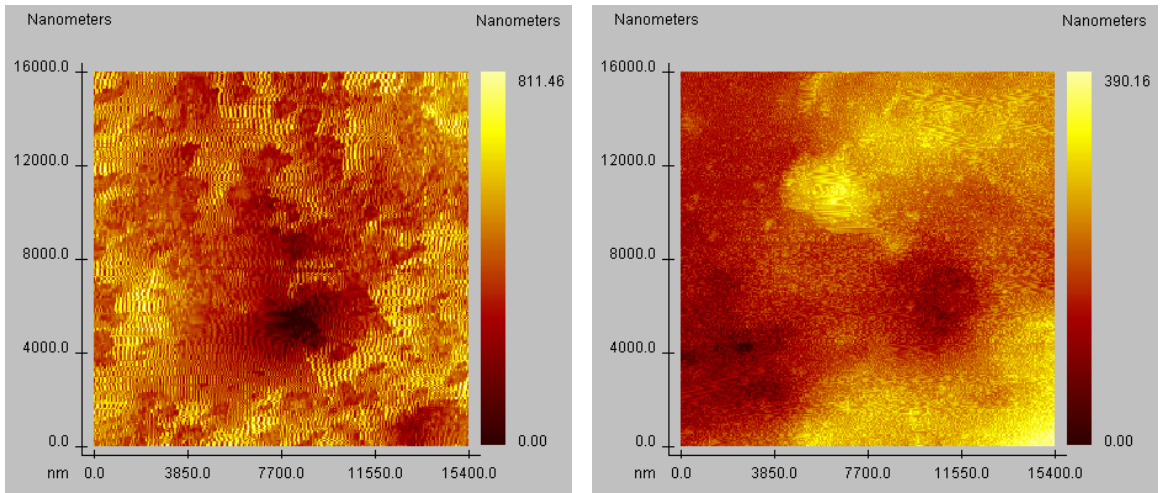


SOY 169 3% REPRODUCIBILITY

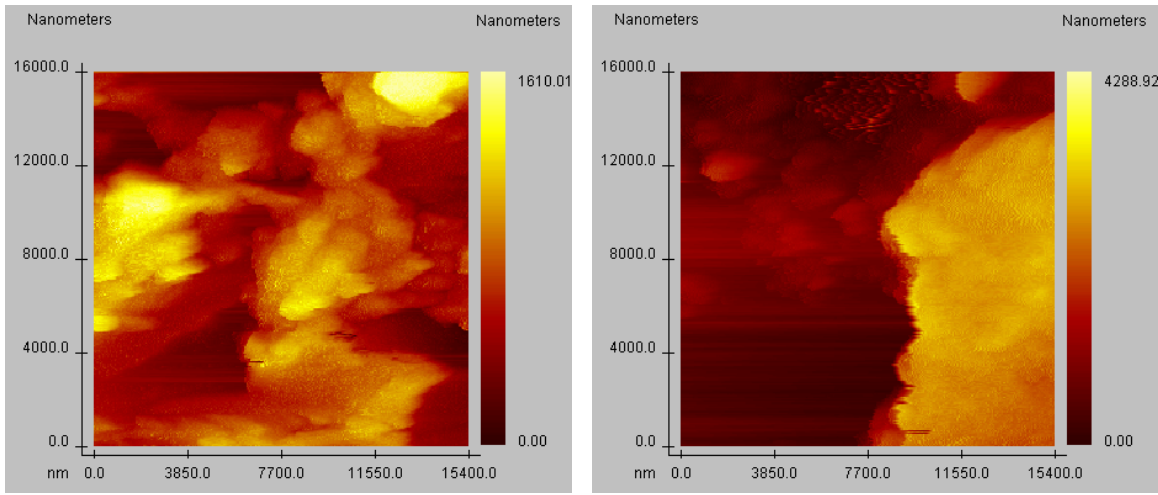
B



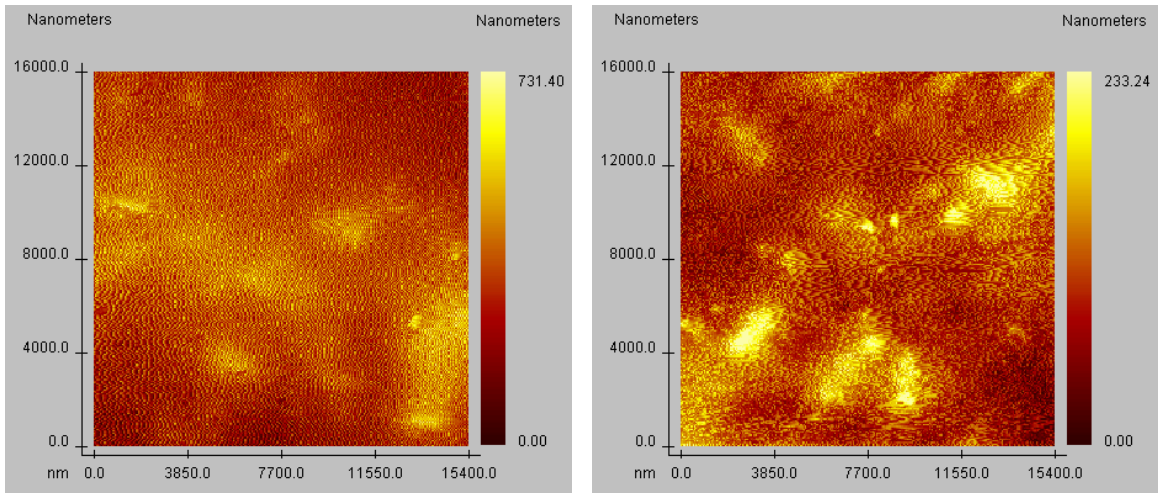
IRREGULARITIES IN SURFACE ROUGHNESS (SOY 169 0%) C



IRREGULARITIES IN SURFACE ROUGHNESS (SOY 169 3%) D

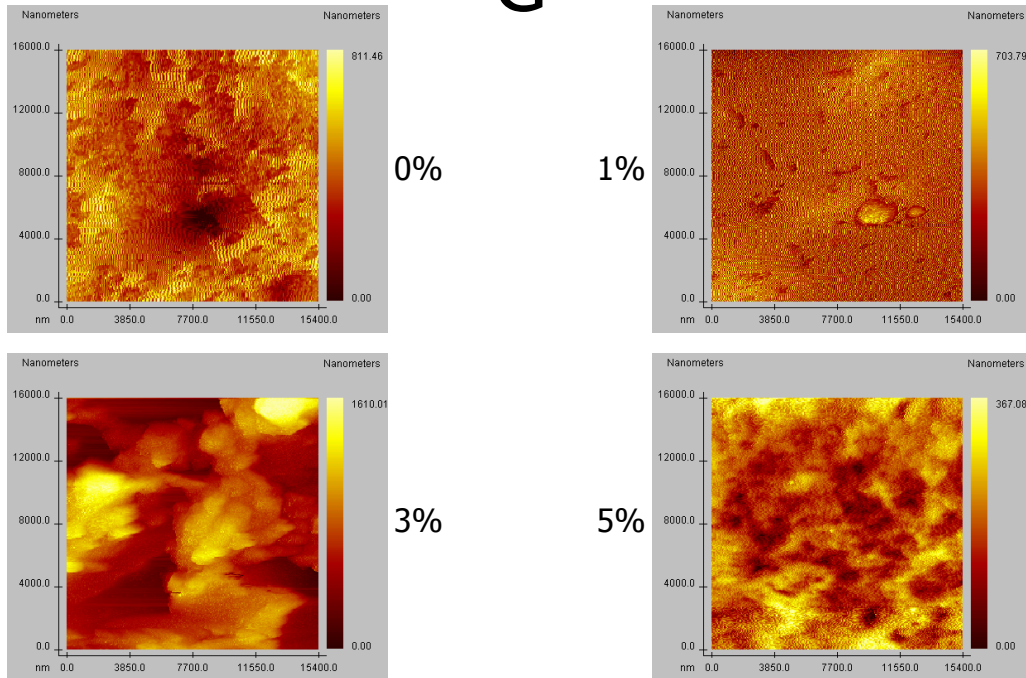


IRREGULARITIES IN SURFACE ROUGHNESS (SOY 201 5%) F



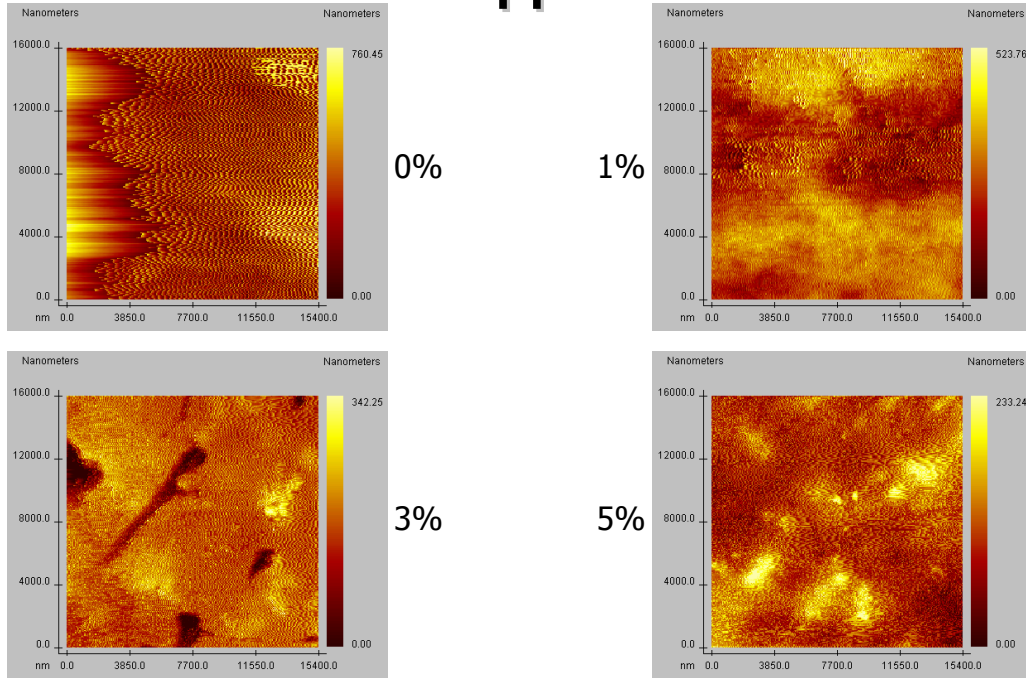
SOY 169 SCANS

G

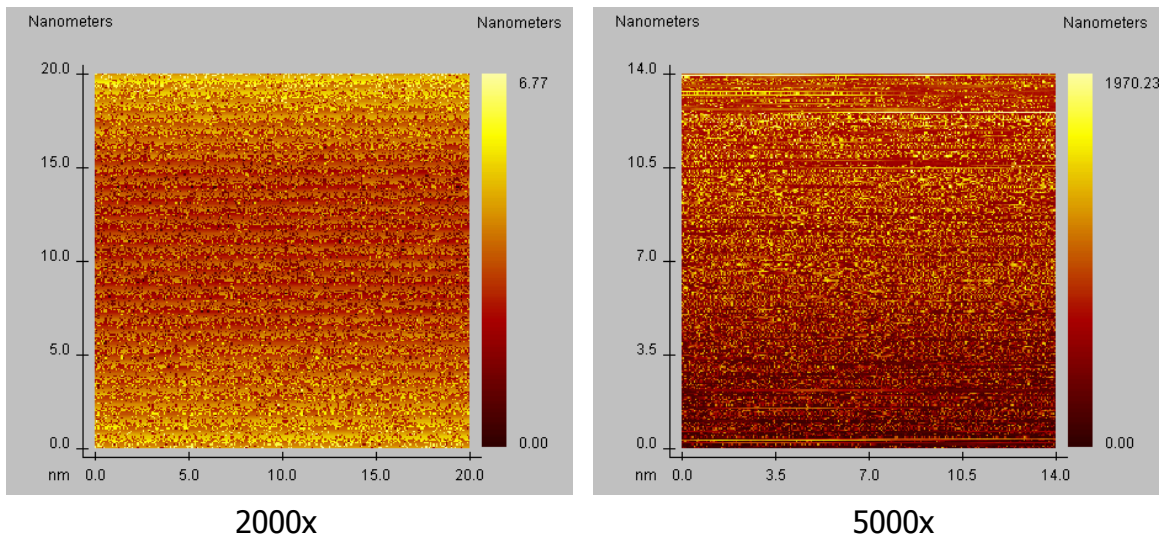


SOY 201 SCANS

H



SURFACE ROUGHNESS TOO GREAT FOR HIGH RES SCANS (I)



7. Discussion of Results

As you look at pics A and B you will notice that there is a very distinguishable similarity between the each set of pictures. There are certain surface features that are similar in each set of pictures. This shows that there is a reproducibility to the pictures and that the AFM is giving valid data.

8. Conclusion

The sample roughness varies randomly along sample surface area. This shows that the samples surface could be due to the mold's texture and preparation of the sample rather than the composition of the sample. The variation of the samples with a surface scan couldn't definitively be attributed to composition.

9. Acknowledgement

- ❖ Dr. David Kuehn
- ❖ Mr. Michael Knop
- ❖ Rama Etekallapalli
- ❖ Dr. Chuck Blatchley

❖ Dr. Ibeh Christopher C, Director, CNCMM

10. Reference

1. http://en.wikipedia.org/wiki/Atomic_force_microscope
2. http://www.unitedsoybean.org/newuses/targets_soybased_plastics.html
3. Briell, Bob, Nanoclays – Counting on Consistency <http://www.nanoclay.com/>
4. <http://www.nanoclay.com/gmrelease.pdf>
5. Sherman, Lilli, M, “Nanocomposites: A Little Goes A Long Way”, *Plastics Technology*, June 1999
By, Senior Editor
6. Rama Etekallapalli, “Bio-based Polyurethane Nanocomposites”, *Nanocomposites Symposium summer 2005*, Pittsburg State University, Kansas

11. Appendices:

Appendix A

Equipment used

1. Isotemp® Programmable oven, Fisher Scientific Inc., model 851F
2. Digital Vernier Calipers, Mitutoyo make, model CD-10C, Range – 100mm
3. Digital balance, Metler® Toledo model PR503, max 510g
4. Bench band saw, Delta make, model 28-185
5. Carbon Steel band saw blade, Ridgid power tools, 56 ¼ “
6. Universal Testing machine, MTS systems corporation, model QTest, Speed – 508mm/min, Load – 1250N, MTS Pneumatic grips, Test works QTest ver 2.01 software used
7. Resil Impactor, Ceast Inc., Model 6957.000MN1, Power 165 kg
8. Notcher for plastics, Tinius Olsen, Model 899 Automatic Specimen
9. Differential Scanning Calorimeter DSC 2910, TA Instruments Inc.,
10. Thermomechanical Analyzer TMA 2940, TA Instruments Inc.,
11. Thermogravimetric Analyzer TGA 2050, TA Instruments Inc.,
12. Dielectric Analyzer DEA 2970, TA Instruments Inc.,

13. FT-IR Spectrometer, Perkin Elmer model Spectrum 1000
14. Sonicator, Fisher Scientific, Model FX-15
15. Atomic Force Microscope
16. Wide angle X-ray Diffraction
17. Optical Microscope

Materials used

1. Soypolyol 169, KPRC, OH = 169, EW = 328 and viscosity 5000cps/25 °C.
2. Soypolyol 201, KPRC, OH = 201, EW = 276 and viscosity 12000 cps/25 °C.
3. Cloisite®10A, Southern Clay Products Inc., Sp gravity 1.90 g/cc, % moisture < 2%.
4. MDI, 4-4-Methylenebisphenyl isocyanate, EW = 125, Mp = 42 to 44°C
5. Methanol (CH₄O), Fisher Scientific, CAS#67-56-1, Lot#043359, UN1230, viscosity 0.55cps @ 20°C
6. Methyl ethyl ketone (C₄H₈O), Fisher Scientific, CAS#78-93-3, Lot#991998, UN1193, viscosity 0.41cps @ 20°C
7. Acetone (C₃H₆O), Acros Organics, CAS#67-64-1, Lot#B0506911, UN1090, viscosity 0.32 mPa s @ 20°C
8. Toluene (C₇H₈), Fisher Scientific, CAS#108-88-3, Lot#050672, UN1294, viscosity 0.59 cps @ 20°C
9. Distilled water (H₂O) Na⁺ free, Wal-Mart

Sample compositions:

Since both the OH number of the polyols and the Equivalent Weight of the diisocyanate were known, the amount of MDI (g) was determined by first calculating the Equivalent Weight of the polyols and then the weight of diisocyanate using the pre-determined weight of the polyols (30.0 g). The molecular weight of the polyols is related to the OH number of the polyol (MW = 3 x OH#). Thus, the molecular weight of the polyols was 507 g/mol (SOY169) and 603 g/mol (SOY201). Refer Appendix B for formulations.

Designation of samples:

The designation of the samples was made according to the following rule: the first 3 characters represent the commercial name of the polyol (SOY), followed by the OH number of the polyol; followed by the concentration of nanoparticles in the polyurethane nanocomposite (0, 1, 3, or 5%). The letter “M” stands for the solvent media methanol, similarly, A for acetone, MEK for methyl ethyl ketone, H for water. The final suffix A or B states that during the synthesis of the sample, method A or method B was used.

Example, **Soy169 – 0M – A**

Sample Preparation

Two different methods are used to prepare the polyurethane nanocomposites.

Method A: Mechanical stirring

The nanoclay filler was mixed with solvent media and stirred at high speed for 24 hours. Polyol was added to the mixture and continued the stirring for 16 hours. The solvent

media is removed by distillation under low and high vacuum. Diisocyanate was added to the mixture and mixing was done under vacuum in the hot water bath. The mixture was then poured into a preheated mold (100°C) and leaves it overnight for curing to obtain 1 mm thick sheets.

Appendix B Formulations:

Equivalent weight of polyols:

$$\text{Soypolyol - 169} \quad E_w = \frac{56.1 \times 1000}{\text{OH number}} \left[\frac{\text{mg KOH / eq}}{\text{mg KOH / g polyol}} \right] = \frac{56110}{169} = 332 \frac{\text{g polyol}}{\text{eq}}$$

$$\text{Soypolyol - 201} \quad E_w = \frac{56.1 \times 1000}{\text{OH number}} \left[\frac{\text{mg KOH / eq}}{\text{mg KOH / g polyol}} \right] = \frac{56110}{201} = 279 \frac{\text{g polyol}}{\text{eq}}$$

Weight of diisocyanate:

$$\text{Soypolyol - 169} \quad \frac{W}{E_w} = \frac{30.0 \text{ g polyol}}{332 \text{ g polyol / eq}} = 0.09 \text{ eq}$$

$$\text{MDI} \quad W = 0.09 \text{ eq} \times E_w = 0.09 \text{ eq} \times 125.0 \text{ g polyol / eq} = 11.47 \text{ g (+2\% excess = 1.02 g)}$$

$$\text{Soypolyol - 201} \quad \frac{W}{E_w} = \frac{30.0 \text{ g polyol}}{279 \text{ g polyol / eq}} = 0.10 \text{ eq}$$

$$\text{MDI} \quad W = 0.10 \text{ eq} \times E_w = 0.10 \text{ eq} \times 125.0 \text{ g polyol / eq} = 12.75 \text{ g (+2\% excess = 1.02 g)}$$

The Tables 1 and 2 present the composition of the two series of samples synthesized.

Table 1. Composition of the samples of polyurethanes for the series Soy169 (Solvent – Methanol; Methylethylketone; Water; Acetone)

Designation	Nanoclay content (%)	Nanoclay (g)	Polyol (g)	Diisocyanate (g)
Soy169 – 0M – A	0	0	30	11.5
Soy169 – 1M – A	1	0.41	30	11.5
Soy169 – 3M – A	3	1.34	30	11.5
Soy169 – 5M – A	5	2.07	30	11.5

Table 2. Composition of the samples of polyurethanes for the series Soy201

(Solvent – Methanol; Methylethylketone; Water; Acetone)

Designation	Nanoclay content (%)	Nanoclay (g)	Polyol (g)	Diisocyanate (g)
Soy201 – 0M – A	0	0	30	12.75
Soy201 – 1M – A	1	0.42	30	12.75
Soy201 – 3M – A	3	1.28	30	12.75
Soy201 – 5M – A	5	1.64	30	12.75