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SYNTHESIS AND CHARACTERIZATION OF CALCIUM CARBONATE NANOPARTICLES AND THEIR EFFECT ON VEGETABLE OIL BASED POLYURETHANE ADHESIVE[1]

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ABSTRACT

In the accompanying task, CaCO3 Nanoparticles (CCNPs) were set up by controlled precipitation of soaked carbonate and calcium nitrate fluid arrangements. The portrayal of the Nanoparticles was finished utilizing SEM, TEM and XRD methods. XRD was utilized to decide the crystallite measure, SEM was utilized to decide the surface morphology and TEM was utilized to decide the molecule size of the CaCO3 Nanoparticles. It was discovered that CaCO3 of 46nm crystallite estimate and cuboidal morphology, having normal molecule size of 82.71 nm were acquired.

The prepared $CaCO_3$ Nanoparticles were incorporated in Vegetable Castor-Oil based Polyurethane adhesive in different concentrations and their effect on mechanical properties of the Adhesive was studied by comparing the Lap Shear Strength of adhesive on a wood substrate using a UTM machine.

INTRODUCTION

Polyurethane adhesives, both water-borne and solvent based, are well known for their properties and are high-performance adhesives. Polyurethanes are prepared by reacting isocyanates with hydroxyl-containing compounds like polyols. By modifying the functionalities of the isocyanates and the polyols, the extent of cross-linking and hence the mechanical properties of the adhesive can be modified. The following properties of PU adhesives make them favourable:

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1. Excellent adhesion properties
2. The curing speed of adhesive can be modified according to the manufacturer
3. The low-temperature performance of PU Adhesives is excellent
4. They have High Heat and Chemical Resistance
5. Their bond strength is very high and they also have low shrinkage.

It has been observed that the PU adhesives made from Petrochemicals are costly and non-biodegradable. Thus, to prevent such problems, biomaterial-based PU adhesives have gained the attention of researchers and scientists. Castor oil is a naturally occurring triglyceride of ricin oleic acid and was employed by us for the synthesis of PU adhesive.

It was observed that the mechanical properties of Castor-oil based PU adhesive depended largely on the NCO/OH molar ratio due to higher or lower cross-linking of reaction. It has been observed in previous research that the mechanical properties of PU adhesive could be altered by the addition of filler materials. Common fillers used in PU are talc, silica, carbon fibre, clay, $CaCO_3$ and TiO_2. Fillers improve the following properties of the PU adhesives:

1. Improved adhesion properties
2. Better resistance to ageing
3. Reduced cost
4. Better mechanical and thermal properties of adhesive

Calcium Carbonate Nanoparticles(CCNPs) have been widely used as filler materials for papermaking, coatings, plastics, adhesives and agriculture. Reasons for usage of CCNPs as a filler for paper include:

1. Improving printing quality of paper by changing smoothness and ink absorption
2. Formation and sheet structure is improved
3. Dimensional stability
4. Texture of paper is improved
5. Appearance of paper also improves
6. Cost of paper is also reduced

CCNPs are also used as fillers in plastic industry. Polymer composites use CCNPs as a filler, mainly in rigid and plasticized PVC, unsaturated polyesters, polyethylene and polypropylene.

CCNPs act as a filler in coatings and enhances properties such as:

1. Weather resistance
2. Anti-corrosion
3. Rheological properties
4. Lower abrasiveness of coating

CaCO3 is additionally utilized as a part of farming in composts where CaCO3 keeps up the pH estimation of the dirt. It is likewise utilized as a calcium supplement in creature feedstock. As examined in resulting pages, we have contemplated the impact of CCNPs as a filler material in cements, especially focussing on mechanical properties.

WHY ARE CCNPs BETTER AS FILLER MATERIALS FOR ADHESIVES THAN REGULAR (MICRO-SIZED) CACO3 PARTICLES?

In case of regular sized particles, there is a tendency of agglomerations or islands or clusters of the material to be formed which is reduced in the case of nanoparticles. Due to these agglomerations, there is non-uniformity and generation of local stresses also takes place. Thus, CCNPs will exhibit better properties as fillers compared to regular size $CaCO_3$ particles.

It is also important to note that the Calcium Carbonate exists in three polymorphs, namely Calcite, Vaterite and Aragonite. The presence of inhibitors like surfactants, contaminants and composites may hinder the formation of crystals. The following table depicts the shape and the existence of various polymorphs.

POLYMORPH OF $CaCO_3$	**BIOLOGICAL EXISTENCE**	**NON-BIOLOGICAL EXISTENCE**	**SHAPE**
CALCITE	Very common	Very common	Rhombohedral
ARAGONITE	Very common	Rare	Needle-like
VATERITE	Rare	Very rare	Hexagonal
NON-CRYSTALLINE	Rare	Non- existent	-

It should be noted that Calcite is the most thermodynamically stable and Vaterite is the least thermodynamically stable among the 3 polymorphs and all polymorphs convert into calcite form when subjected to heat.

In the venture, CCNPs were orchestrated by controlled precipitation of Saturated Carbonate and Calcium Nitrate watery arrangements. The portrayal of CCNPs was finished utilizing XRD, SEM and TEM. CCNPs were consolidated in the PU cement and Mechanical Lap-Shear Testing was finished by applying cement on a wood substrate. The relative mechanical properties of cement on expansion of CCNPs in various sums were considered.

EXPERIMENTAL WORK

CHEMICALS REQUIRED

1. Sodium Carbonate (Na_2CO_3)
2. Sodium Hydroxide (NaOH)
3. Calcium Nitrate Tetra hydrate ($Ca(NO_3)_2.H_2O$)
4. Castor Oil having Hydroxyl value of 160
5. Methylene Diphenyl Diisocyanate
6. Dibutyltin Dilaurate (DBTDL)
7. Methyl Ethyl Ketone
8. Distilled water

APPARATUS REQUIRED:

1. Magnetic stirrer with Heating element
2. Beakers
3. Dropper
4. Burette
5. Stopwatch/ Wrist watch
6. Thermometer
7. Funnel
8. Filter/Whatman Paper
9. Weighing balance

EXPERIMENTAL PROCEDURE:

Preparation of CCNPs by controlled precipitation of saturated carbonate and calcium nitrate aqueous solutions:

1. 0.1M Sodium Carbonate, 0.2 M Sodium Hydroxide and 0.18M Sodium Nitrate aqueous solutions were prepared in deionised water and were added to each other and mixed for 1

minute to ensure solubility. Sodium Hydroxide was added to maintain an alkaline pH suitable for Calcium Carbonate precipitation and Sodium Nitrate was added to reduce solubility of Calcium Nitrate by Common-ion effect.

2. Calcium Nitrate was dissolved in distilled water to give a 0.1M aqueous solution. The two aqueous solutions were ready for mixing.
3. The Sodium Carbonate solution was placed on the Magnetic Stirrer and the Calcium Nitrate solution was added to it dropwise using a burette or a dropper. The mixing time was varied at constant temperature and the temperature was varied for a single mixing time to get 5 samples of CCNPs.
4. The temperature was measured using a scientific thermometer and the particles were obtained by filtering the above solution using filter/whatman paper and drying the particles for 24 hours.
5. Using the above 4 steps, CCNPs were obtained which were ready for characterisation. The amount of CCNPs needed for characterisation and incorporation in PU adhesives was measured and the amount was obtained by keeping the concentration of above reactants constant but by changing volume of reactants used.
6. After the preparation of CCNPs, their characterization was done using XRD, SEM and TEM analysis as discussed below.

PREPARATION OF CASTOR-OIL BASED PU ADHESIVE:

1. Calculated amounts of Polyol was added along with Methyl Ethyl Ketone and Dibutyl Tindilaurate (DBTDL) in a beaker and stirring was done for 5 minutes.
2. For preparation of CCNP incorporated adhesive, 1%, 2%, 3%, 4% (by weight of polyol) was added to the beaker and further stirring was done to dissolve the CCNPs.
3. Calculated amount of MDI was added to the beaker and stirring was done till contents became viscous.
4. The adhesive were applied over an area of ($25x30mm^2$) between two wooden substrates having dimensions ($300x25x3mm^3$) and was placed under a defined load for 24 hours for curing of adhesive.
5. The lap shear testing to determine adhesive strength for the above adhesive was performed later in accordance to ASTM standard ASTM D 906-82

CHARACTERISATION AND RESULTS OBTAINED:

The preparation of CCNPs was done by controlled precipitation of saturated carbonate and calcium nitrate aqueous solutions. The yields obtained and the conditions were as follows:

Variation of temperature at constant mixing time:

SAMPLE NO.	TEMPERATURE (in Celsius)	MIXING TIME (in Minutes)	YIELD OBTAINED (in Grams)
Sample 1	32	15	0.221
Sample 2	43	15	0.301
Sample 3	65	15	0.335

Variation of mixing time at constant temperature:

SAMPLE NO.	TEMPERATURE (in Celsius)	MIXING TIME (in Minutes)	YIELD OBTAINED (in Grams)
Sample 4	32	5	0.228
Sample 5	32	10	0.291
Sample 6	32	15	0.221

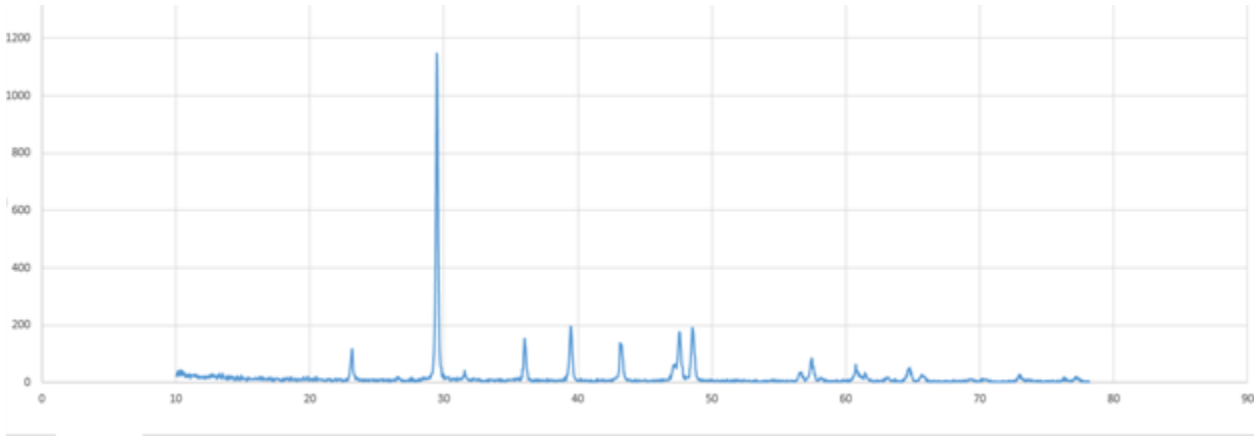
Another sample was prepared for XRD in which molarity of reacting components was kept same but volume and weight of all reacting components was increased by 10 times. The mixing time was taken to be 15 min at 32 degrees Celsius. The yield of this **Sample 7** was **3.49 grams.**

INFERENCES:

1. **It was observed that the yield of the CCNPs increased as the temperature was increased.**
2. **No trend of the yield of the CCNPs with variation in mixing time was observed.**

XRD Analysis:

The XRD analysis of the CCNPs was done to get the crystallite size of CCNPs. The XRD plot obtained as follows:



The determination of crystallite size using XRD analysis was done using the Scherer's equation:

$$T = K\lambda / \beta\cos\theta$$

Where:

T*:* mean size of the crystalline domains, which may be smaller or equal to the particle size

K: dimensionless shape factor, K=0.9

λ : the X-raywavelength

β:Full width at half maxima (generally expressed in radians)

θ :Bragg angle.

By our XRD analysis, it was found that:

λ =0.154nm (X-Ray wavelength)

β=0.0031

θ=29.8/2=14.9 degrees

Using Scherrer's equation, we get

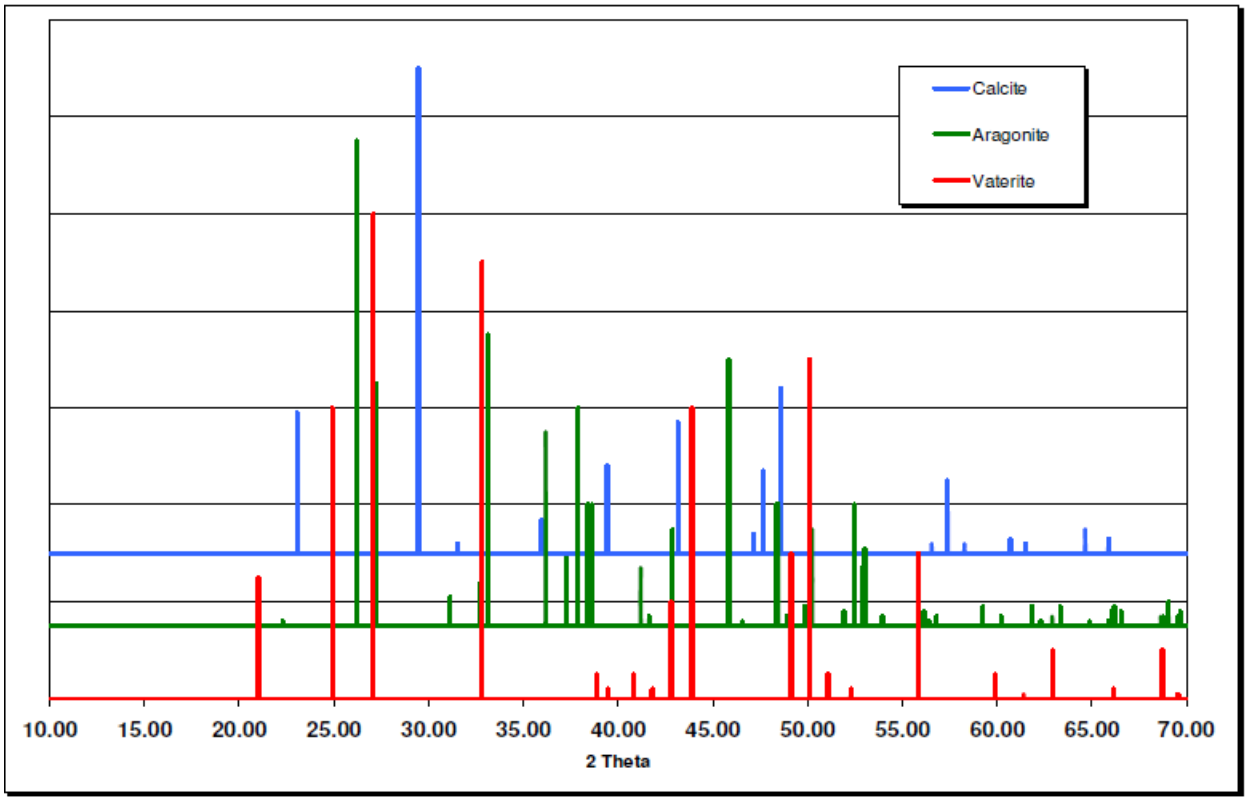
T= (0.9x0.154)/ 0.0031xcos (14.9 deg)

Or T= 0.1386/0.00299

Or **T= 46nm (Approx.)**

INFERENCES:

1. **Thus, by XRD analysis it has been confirmed that the particles we have obtained are of Nano-range and the crystallite size of the CCNPs was found to 46nm.**



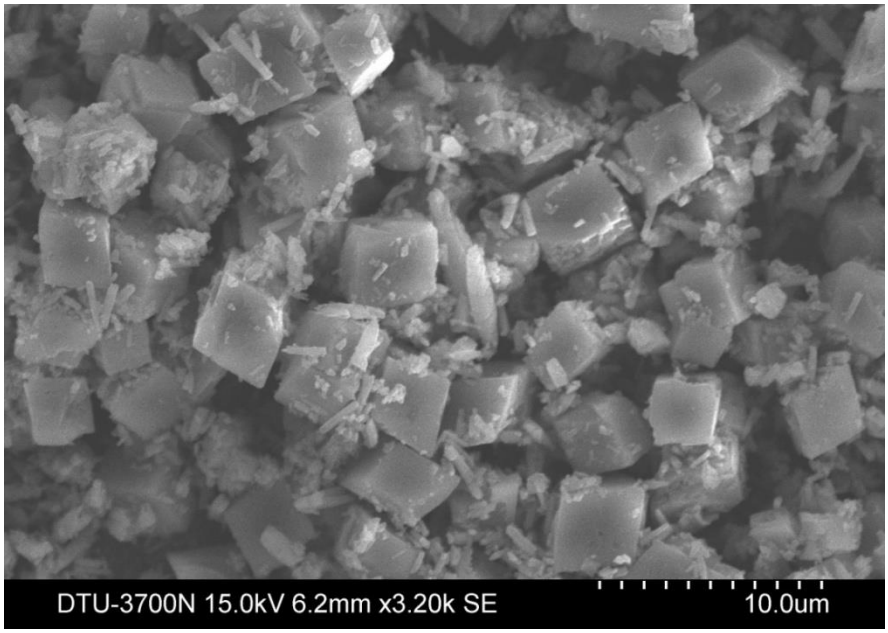
XRD DATA OF POLYMORPHS OF $CaCO_3$

2. **The XRD analysis of the CCNPs was also compared with the XRD analysis of the polymorphs of CCNPs already available in literature and comparison was done. The comparison showed us that the Calcite form of $CaCO_3$ was obtained by our experimental method.**

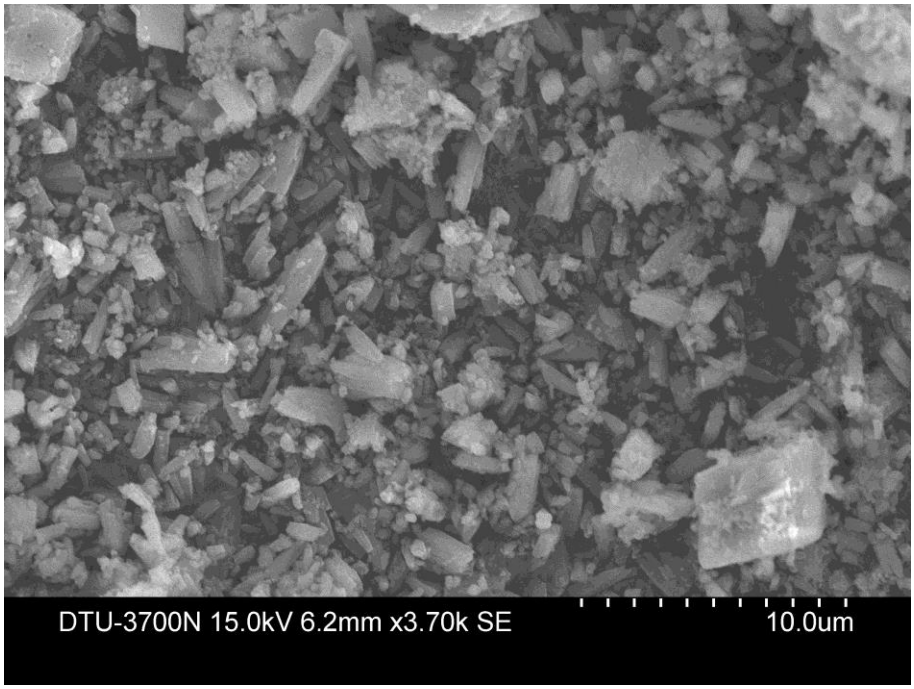
SEM Analysis:

The SEM Analysis of the CCNPs was done to determine the surface morphology of the CCNPs obtained:

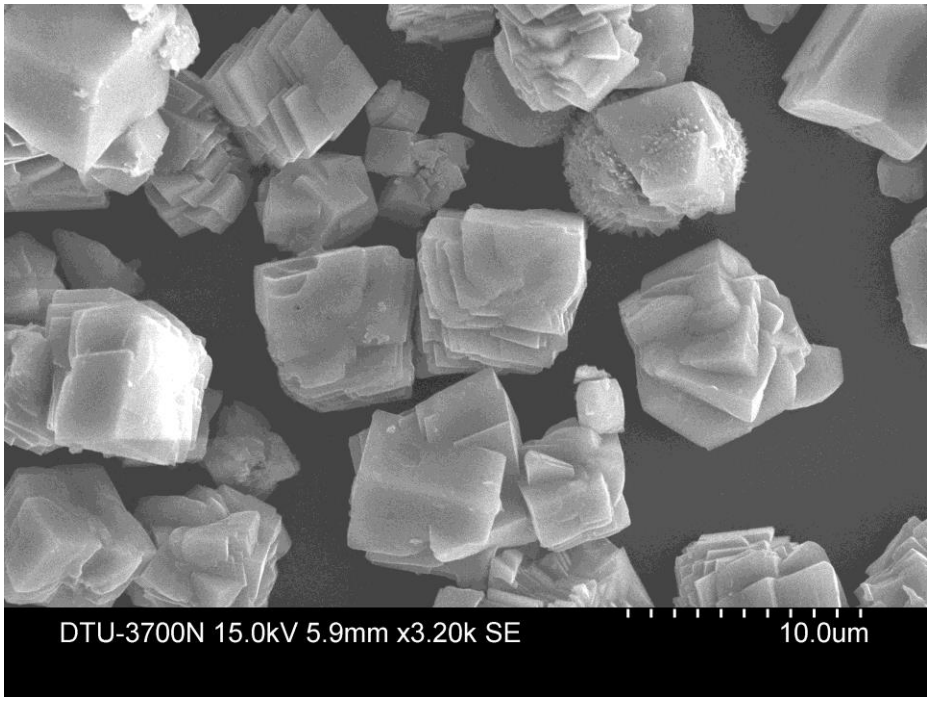
Sample 1:



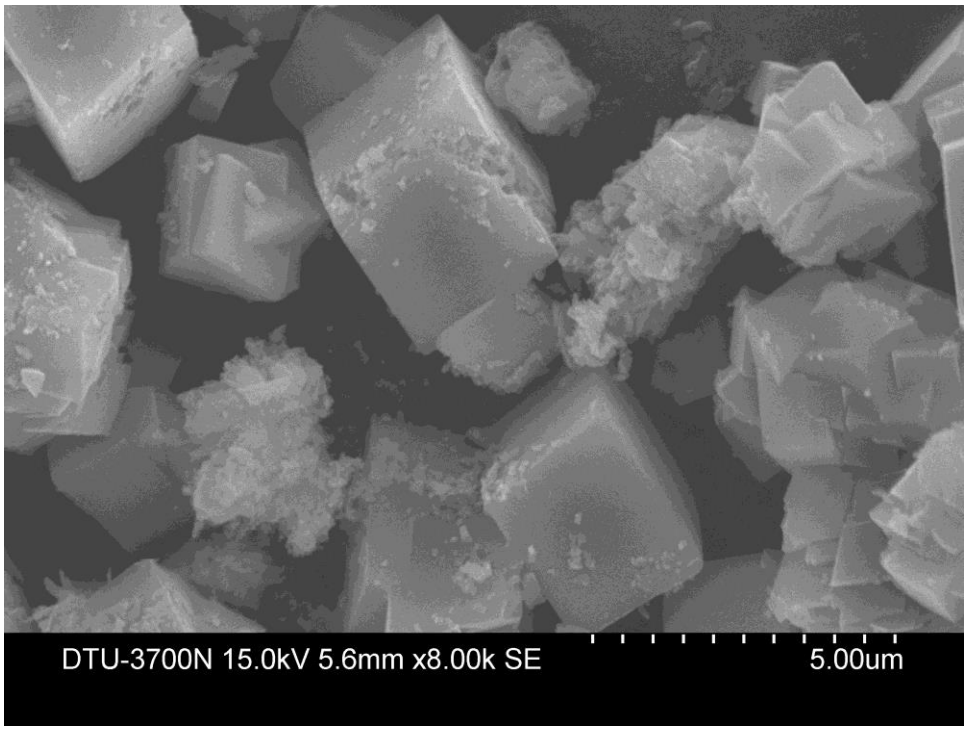
Sample 2:



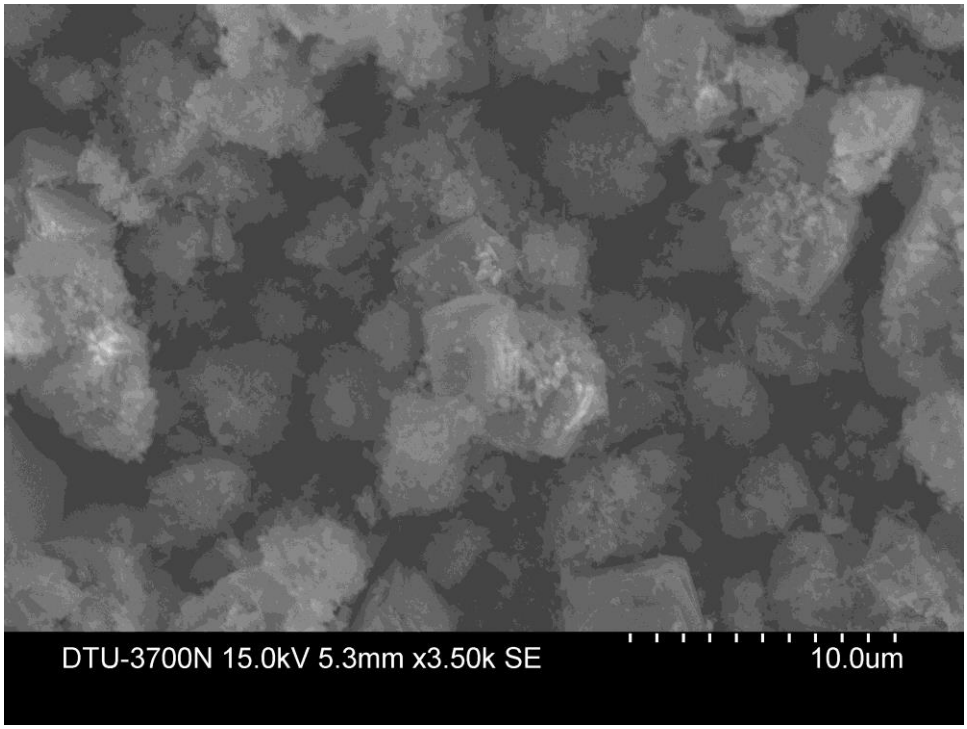
Sample 3:



Sample 4:



Sample 5:

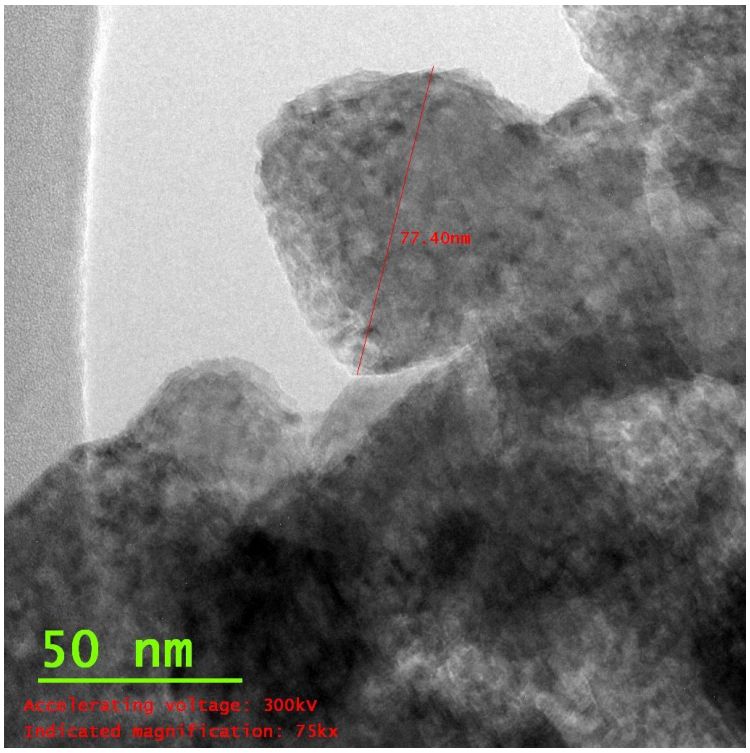


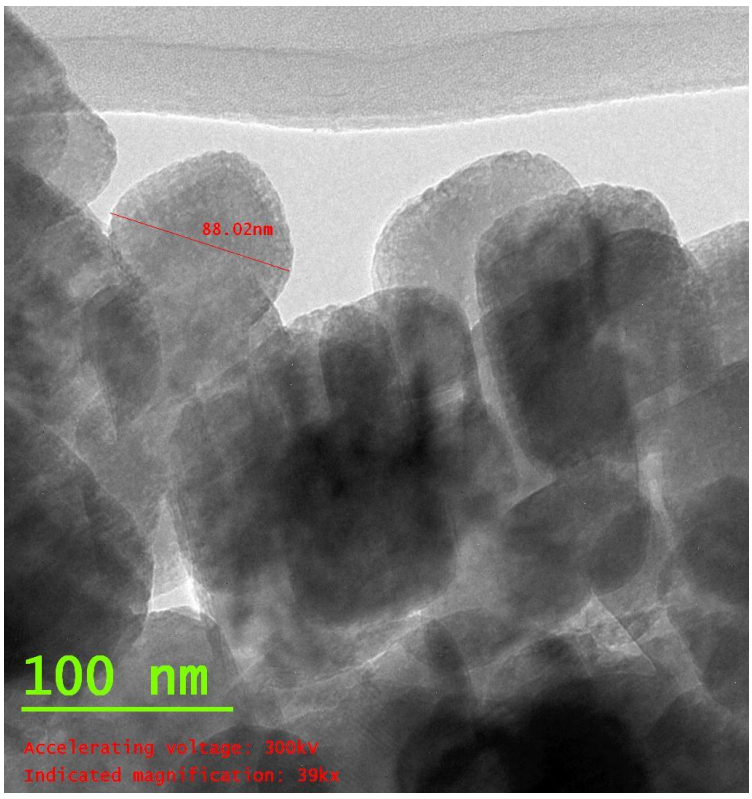
INFERENCE: It was observed by SEM that the morphology of the CCNPs was cuboidal and no Nano cracks or bubble formation was observed on the surface of the nanoparticles.

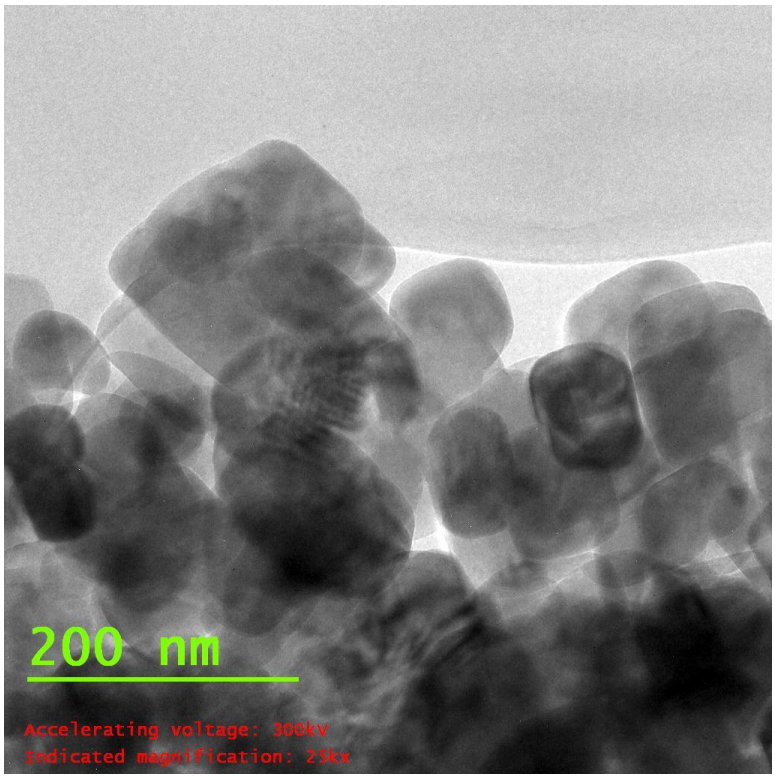
The above nanoparticles were then incorporated in adhesive and the lap shear testing was done in accordance to ASTM Standards ASTM D 906-82.

TEM Analysis:

The TEM Analysis of the CCNPs was done to determine the particle size of the CCNPs obtained:


77.40nm
50 nm
Accelerating voltage: 300kV
Indicated magnification: 75kx


88.02nm
100 nm
Accelerating voltage: 300kV
Indicated magnification: 39kx



(Courtesy: JamiaMilliaIslamia University)

INFERENCE:

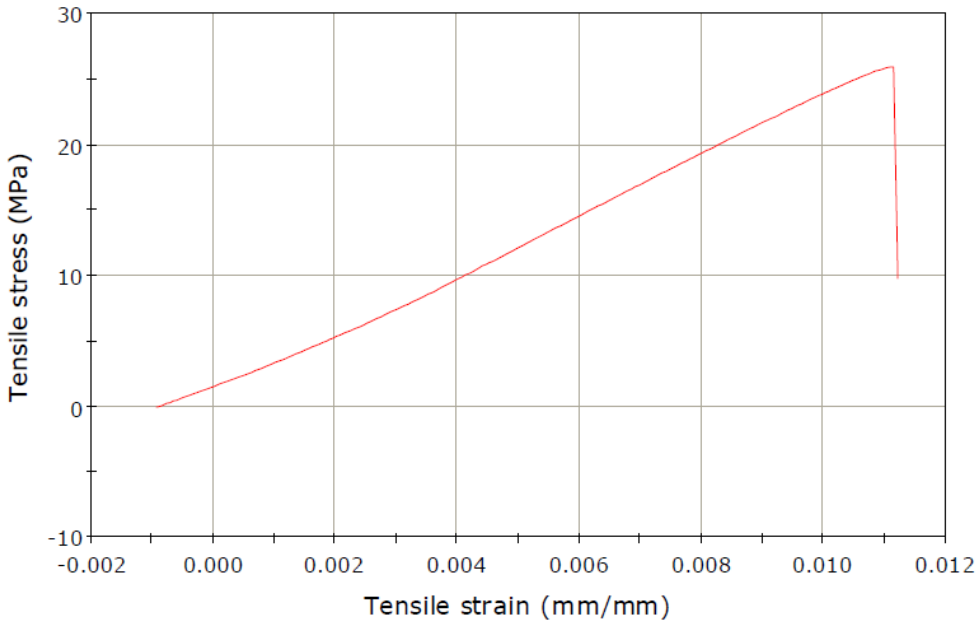
1. **The average particle size of the CCNPs was found to be (88.02+77.40nm)/2= 82.71nm**

LAP SHEAR TESTING:

The lap shear testing of the neat PU Adhesive, PU adhesive filled with 1%,2%, 3% and 4% CCNPs (by weight of Polyol) was done as explained in the experimental section and in accordance to ASTM D 906-82.

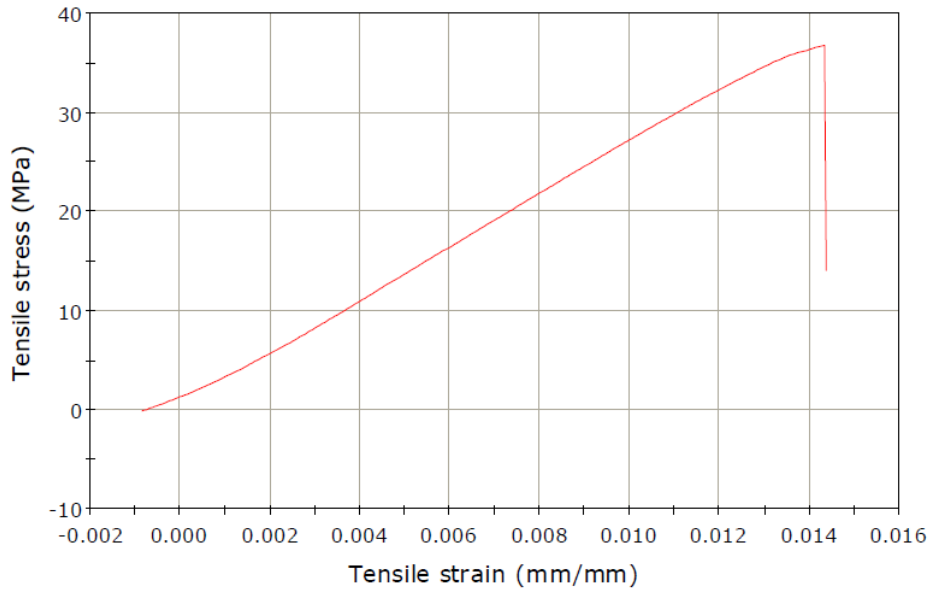
The results of the Lap shear test are explained below:

NEAT PU Adhesive (without any CCNPs added):



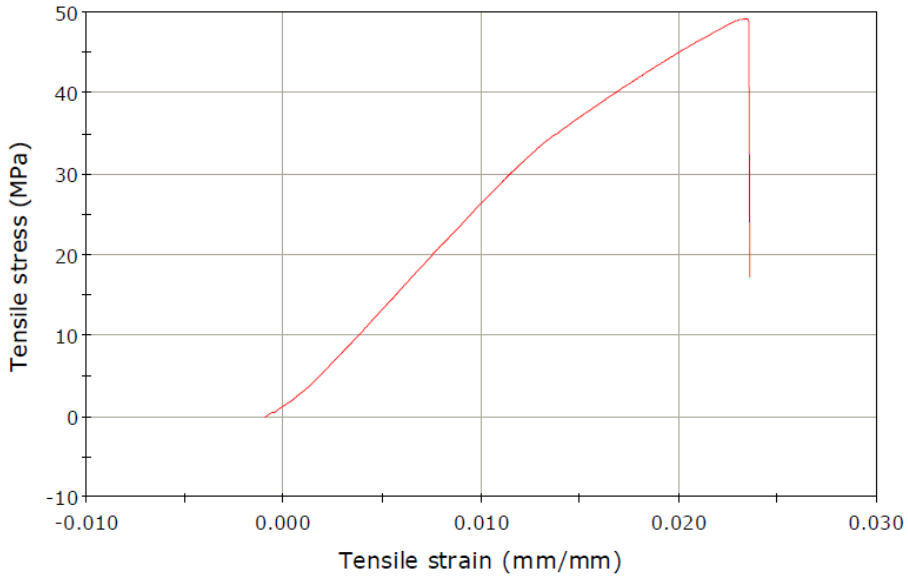
Lap Shear Strength=26 MPa (approx.)

PU filled with 1% CCNPs:



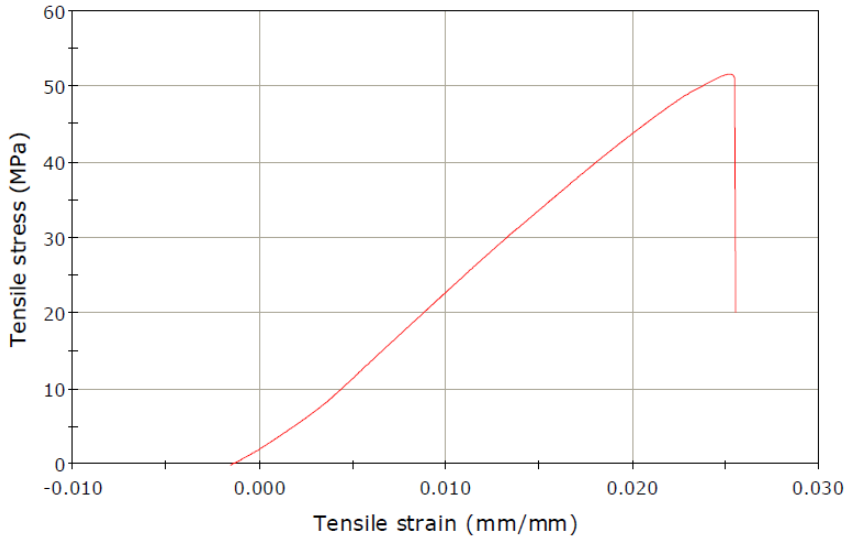
Lap Shear Strength= 37MPa (approx.)

PU filled with 2% CCNPs:



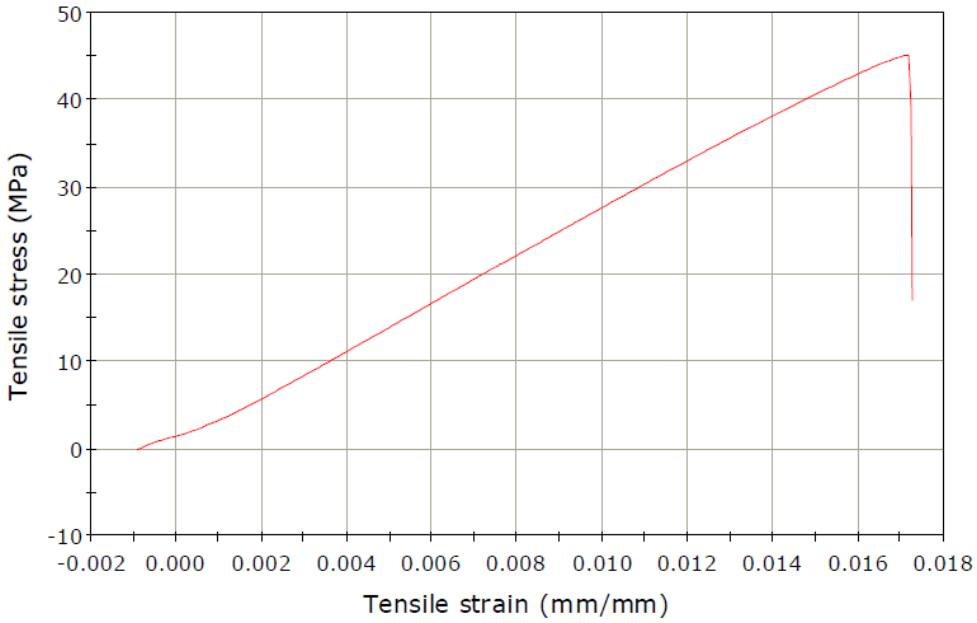
Lap Shear Strength= 49MPa (approx.)

PU filled with 3% CCNPs:



Lap Shear Strength= 51MPa (approx.)

PU filled with 4% CCNPs:



Lap Shear Strength= 45MPa (approx.)

Tabulating above results:

Concentration (by wt. of Polyol) of CCNPs added to PU Adhesive	**Lap Shear Strength (in MPa)**
0% (NEAT SAMPLE)	26
1%	37
2%	49
3%	51
4%	45

INFERENCES:

1. **Incorporating CCNPs upto a concentration of 3% increased the Adhesion strength of PU adhesive.**
2. **After incorporating the CCNPs to a concentration greater than 3%, it was found that the CCNPs do NOT disperse easily in the Adhesive and the Adhesion strength was also found to decrease at concentration of CCNPs greater than 3%.**

RESULTS AND FUTURE SCOPE OF RESEARCH

Castor Oil based Polyurethane adhesive was prepared and CCNPs of Nano-size were incorporated in them. The mechanical properties (namely Lap Shear Strength) of the adhesive increased till the filler was added up to 3% by weight of the Polyol. Above 3%, the CCNPs did not properly disperse and the Lap Shear Strength of the adhesive was diminished. The preparation of the filler, i.e. CCNPs was done by controlled precipitation of Calcium Nitrate and Carbonate aqueous solutions. The crystallite size was found to be 46nm by XRD analysis, which also confirmed that the Calcite polymorph of CCNPs was obtained. The morphology of the particles was found to be cuboidal by SEM analysis and the particle size was found to be 82.71nm using TEM Analysis.

Further research can be done by incorporating several other fillers (like silica, talc) etc of nano-range in the adhesive and doing a comparative study of the mechanical and thermal properties of the adhesive. Development of more efficient adhesives incorporated with these fillers can be done and further attempts to prepare better adhesives can bring fruitful results.

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