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EXPERIMENTAL STUDY AND CHARACTERIZATION OF CONDUCTIVE (NACUO) METAL OXIDE NANOPARTICLE INCORPORATED POLYURETHANE FILMS FOR SENSING APPLICATION.

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Abstract

In this research work sodium doped copper metal oxide nanoparticles prepared by sol-gel technique dispersed in polyurethane matrix synthesized from castor oil have been studied for electro-mechanical property so as to be used for sensing application. This is achieved by recording current conductivity in conductive polyurethane films prepared by prepolymer method with enhancing filler content from 0.5 wt% to 4.0 wt%. The samples were subjected to tensile elongation and change in current conductivity was recorded. The recorded results reveal that Na:CuO-NPs dispersed in polyurethane has the potential to be used as a sensor material to monitor deformation changes or motion sensitivity.

Keywords: Polyurethane, NaCuO, Castor Oil, Sol-Gel.

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1. Introduction:

It is well recorded that the incorporation of conductive metal oxides into a insulating polymers can lead to the development of new polymer materials with enhanced electrical properties. Polymer nano composites used for sensing applications demand enhancement of electrical properties along with mechanical characteristics with easier production techniques. Conductive metal oxide nanoparticles doped into polymers lead to incorporation of inherent conductivity which makes them multi-functional and applicable for use developing sensors and actuators. The basic rule is monitoring of the changes in electrical conductivity in order to measure the deformation levels.[1] The key factor in performance enrichment is credited to the small size of nanofillers leading to large surface area, quantum confinement effect along with strong interfacial interactions [2].

2. Experimental

2.1 Materials

Analytical grade chemicals were procured without any further purification. Castor oil (C₅₇ H₁₀₄ O₉) with Molecular weight of 933.45 g/mol and Hydroxyl Number of 160, Methyl Ethyl Ketone (C₄H₈O with Molecular weight 72.11 g/mol) was procured from S.D. Fine Chem. (Mumbai, India), Toluene-2, 4-diisocyanate (C₉ H₆ N₂ O₂ with molecular weight of 174.16 g/mol) and Dibutyl Tin Dilaurate (C₃₂ H₆₄ O₄ Sn with molecular weight 631.66 g/mol) was procured from TCI Chem (Chennai, India). Cupric Nitrate Trihydrate (Cu(NO₃)₃H₂O), Sodium Nitrate (NaNO₃), Glycine (C₂ H₅ NO₂) and Sucrose (C₁₂ H₂₂ O₁₁) from Himedia laboratory.

Synthesis of Sodium Doped Copper Metal Oxide Nanoparticles

Sodium doped Copper Metal oxide Nanoparticles (Na:CuO-NPs) were prepared by sol-gel method. Cupric Nitrate was used as oxidizer, glycine and sucrose was used as fuel. 1.938 g of cupric nitrate

0.169 g of sodium nitrate, 0.342 g of sucrose and 0.07 g of glycine was dissolved in 200 mL of doubly distilled water. The mixture was stirred for about 5 hours and temperature maintained between 60-70⁰C. When the mixture reaches below 20mL, stirring is stopped and heating continued with increased temperature till we observe gel formation. The obtained solution is further heated to get auto ignited by placing the beaker on Hot Plate and precipitation is observed. The obtained combustion product is transferred to ceramic crucible and left for annealing in muffle furnace at 800⁰C for 1 Hr [2-4].

Synthesis of Polyurethane (PU) Nano Composites

A Three-necked polymerization reactor placed in water bath with mechanical stirrer, and dropping funnel attachment was used along with provision for nitrogen inlet. The reactor was charged with Castor Oil (CO) and Toluene-2,4- diisocyanate (TDI) with 1:1 molar ratio and Methyl Ethyl Ketone (MEK) was the solvent. Air dried at 70⁰C and weighted percentages of fillers 0.5, 1, 2, and 4 wt% was dispersed into the matrix to fabricate the composites. CO and TDI were dissolved in MEK and stirred at temperature of 60⁰C for 1hr under nitrogen blanketing, dibutyl tin dilaurate (DBTL) was added to the mixture and stirred to form the prepolymer. Calculated amount of Na:CuO nanoparticles were added to the prepolymer mixture and sonicated for 30 minutes under inert atmosphere at 60⁰C. The reaction mixture was poured into a glass mold and dried for 12 Hrs at room temperature. Post curing of the mixture was done at 70⁰C for 8Hrs in Hot air oven[5]. Same procedure was repeated with varying amounts of Na:CuO wt% in the PU matrix. Undoped PU specimens were also prepared for reference studies. All the specimens were sized as per test specifications.

Methods

Scanning Electron Microscopy (SEM) was used for observation of Na:CuO NPs distribution in PU Matrix. The SEM surface was analysed after gold sputtering using HITACHI-S-3400N NORAN SYSTEM7 coupled with THERMO SCIENTIFIC energy dispersive X-ray spectroscopy (EDX) (USA). Infra-red spectra (FTIR) of specimens were acquired with FTIR-4100 Fourier Transform Infrared Spectrometer with ATR Attachment (JASCO, Japan). During FTIR, three different points on the film surface were investigated. Using REGAKU Diffractometer (Japan) in the scanning range of 0° – 80° X-ray diffraction (XRD) patterns were recorded. Specially selected samples were only tested for FTIR XRD and SEM Analysis. The samples were examined to tensile loading using computerised UTM machine (International Equipments, Mumbai). For all filler wt% at least three samples were tested. During each test, longitudinal elongation and electrical conductivity were measured. The cross head speed was fixed as 0.6mm/min [6]. For electrical measurements direct current was applied to the electrode contacts using a Keithley 2460 Current Source meter.

Results

Structural and Morphological Characterization of Na:CuO PU Nanocomposites

The FTIR (Fourier Transform Infrared Spectra) for Pristine PU and PU/metal nanocomposite of different filler weight percentage concentration of 0.5, 1.0, 2.0 and 4.0% of Na: CuO is as presented in Figure 1. FTIR Spectra indicates a narrow and strong characteristic band with intensity at 1733 cm^{-1} of the free urethane carbonyl stretching vibration (C=O) region, characteristic peaks of hydrogen bonded –NH groups are observed at $3291\text{--}3362\text{ cm}^{-1}$ indicating successful formation of urethane linkage[5,6]. The peak at 1536 cm^{-1} is due to stretching vibration of –NH

bond, aromatic stretching C-H is observed between $2820\text{--}3040\text{ cm}^{-1}$ with high intensity peaks at 2921 and 2858 cm^{-1} . We could see modest broad band in the range $4000\text{--}3500\text{ cm}^{-1}$ due to O-H stretch vibrations hydroxyl ended compounds [8]. By the addition of Na: CuO NPs the peaks at are observed to be broader at 3365 cm^{-1} with higher intensity with the increase in weight percentage of Nanoparticles. We observed narrow peaks with higher intensity at 1736 , 1600 , 1536 cm^{-1} wavelength indicating metal oxygen stretching. Peaks obtained at 750 , 820 , 876 , 1410 , 1460 cm^{-1} confirm the presence of Na:CuO stretching vibrations[9].

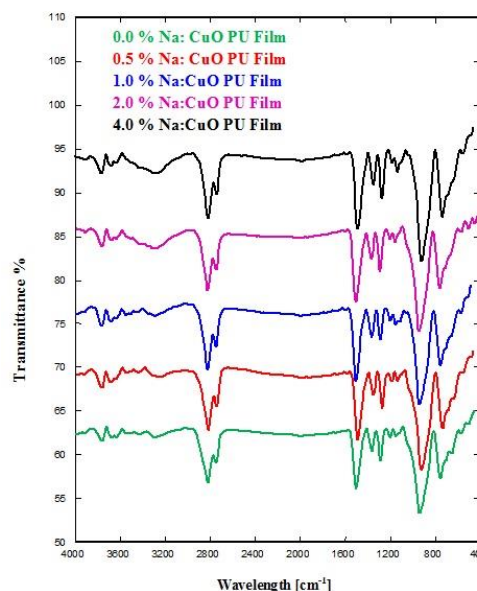


FIGURE 1: FT-IR Spectra of PU-Na:CuO Nanocomposites, with Pristine, 0.5, 1.0, 2.0 and 4.0 wt% NPs loadings.

The XRayDiffraction spectrum of Pristine and filler doped films are presented in Figure 2. It is revealed from the figure that the intensity of peaks increases with increasing weight percentage of nanoparticles, which indicate enhancement of the sample film crystallinity. The Undoped films under investigation show peaks at $2\theta = 20.3^{\circ}$ of the reflection plane with interchain (d) spacing of 4.369 \AA , which confirms the presence of short range regular ordered structure with hard and soft domains and also the presence of

disordered amorphous phase in polyurethane matrix [7]. By the addition of fillers, peaks show broadened nature with higher intensity, which may be due to the stronger interactions between Na:CuONPs and PU Matrix. The doped films show further diffraction peaks at 2θ values of 35.58° and 38.75° and d spacing of 2.521, 2.321\AA confirming the presence of Na:CuO NPs in PU Matrix [3]. We observe a slight shift of 0.5° from the peak of pristine samples towards left may be owing to crystallinity and the area subjected for analysis.

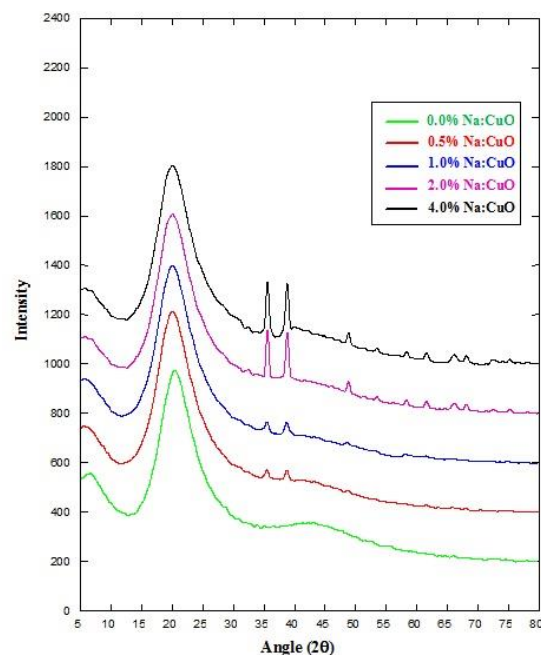


FIGURE 2. XRay Diffraction Spectrum of PU-Na:CuO Nanocomposites, with Pristine, 0.5, 1.0, 2.0 and 4.0 wt% NPs loadings.

Morphological Characteristics

The morphological examination of pristine PU films and Na :CuO doped films were determined by Scanning Electron Microscopy. The image confirms neat PU films with minimal agglomeration (Figure 3a), presence of filler nanoparticles and

uniform dispersion is seen (Figure 3b), the nanocomposite films chosen for study was containing 4.0 wt% filler. Studies by [9] confirm Na doped CuO to exhibit poly crystalline structure and the same was observed in SEM image.

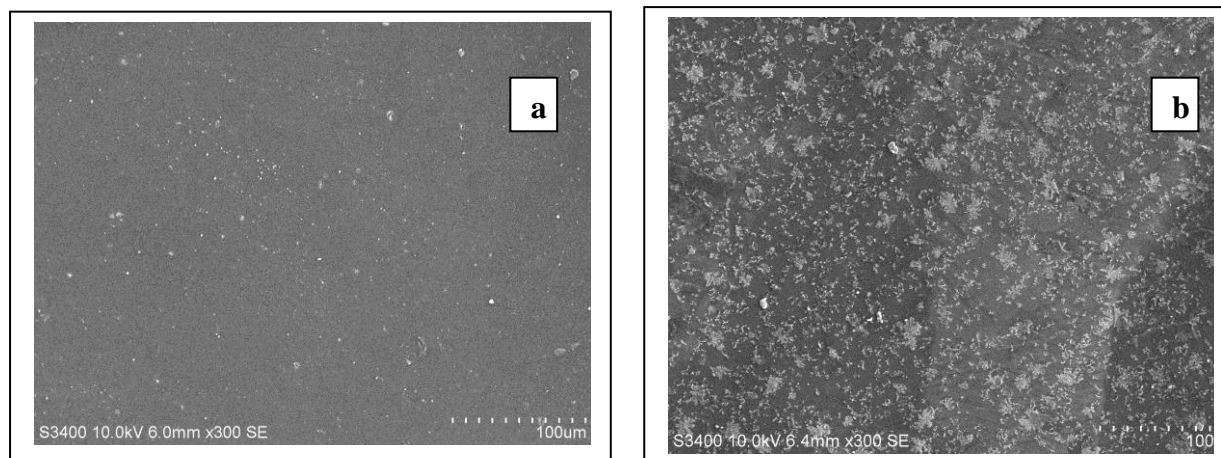


FIGURE 3: a SEM image of pristine PU film b Na:CuO Nps in PU Film.

Element Detection Analysis. The elemental microanalysis composition of the synthesized Polyurethane- Na:CuO nanocomposites were performed by the

Energy dispersive X-ray fluorescence measurements and is represented in Figure 4. EDX analysis verify the presence of Oxygen (O), Nitrogen (N), Carbon (C),

Sodium (Na) and Copper (Cu) where C, O, N form the key elements of polyurethane. The prominent peaks at 0.52, 0.93, 1.04, 8.04 and 8.9 keV were observed. X-ray energy at 0.52 and 0.93 keV represent

emissions from K-shell of oxygen and L-shell of Copper, respectively. X-ray energy at 8.04 and 8.90 keV are the additional emission from core levels of Cu. Energy peak at 1.04 keV is from K-shell of Na [9].

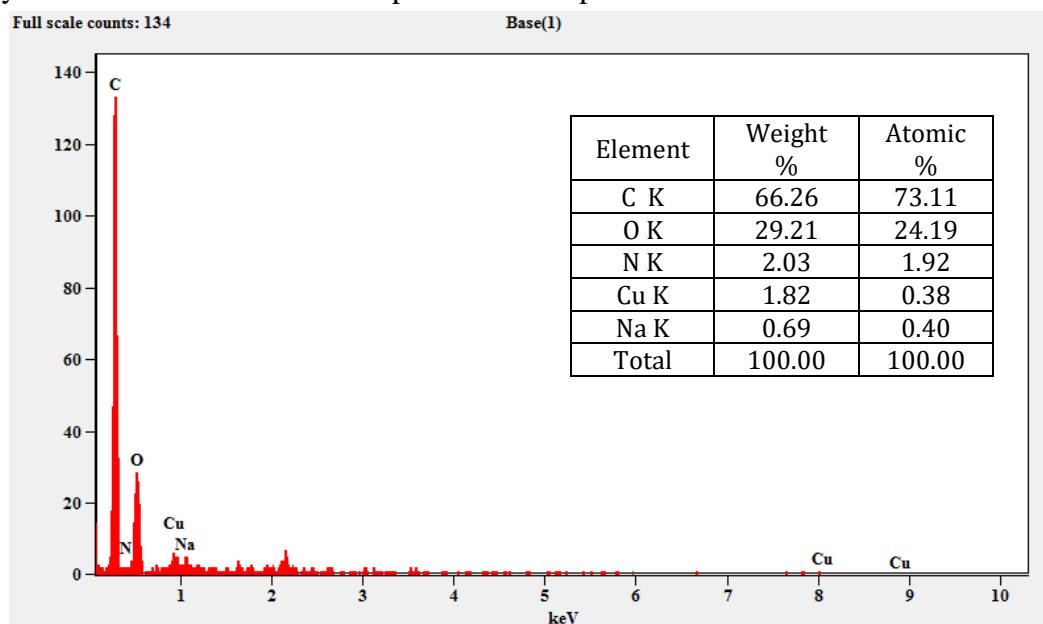


Figure 4: EDX image of Na:CuO NPs Polyurethane Film Nano Composite.

Electro - Mechanical Studies of Nanocomposite Films.

Electro-Mechanical Properties of prepared films specifically tensile strength and elongation at break was noted down. Pure PU films exhibited a tensile strength of 0.152 MPa and 59% elongation at break. With the increase of filler percentage we observed slight improvement in tensile strength and decrement in elongation at break; this is due to the interaction of nanofillers with polymer chains. We studied the behaviour of prepared films for a maximum stretching of 10MM and recorded the relation between longitudinal elongations; current conductivity for different filler

concentration with voltage potential constant at 50 volts is presented in Figure 5 and Figure 6. With the increase in nanofiller weight percent we observed proportionate/linear increase in conductivity [10]. Also we observed that conductivity value in all the films is maximum at zero elongation and decreases as the tensile elongation increases. From figure 6 it is observed that PU films filled with 4wt% nanoparticles show a sharp decrease in current conductivity values after tensile elongation distance of 3.0 MM onwards, this phenomena may be due to agglomeration of fillers in the film and sudden increase in particle to particle distance during stretching.

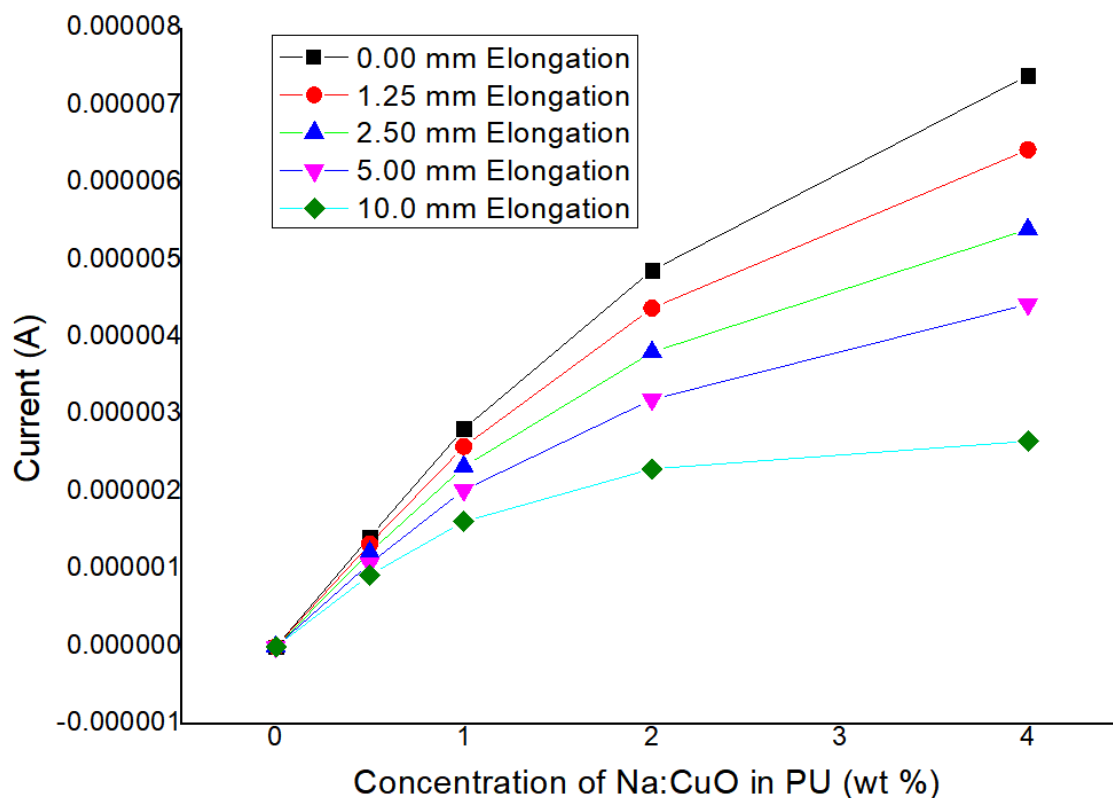


Figure 5: Electro-Mechanical Conductivity Plot of Pristine PU and Na:CuO filled PU Films loaded at 50V potential.

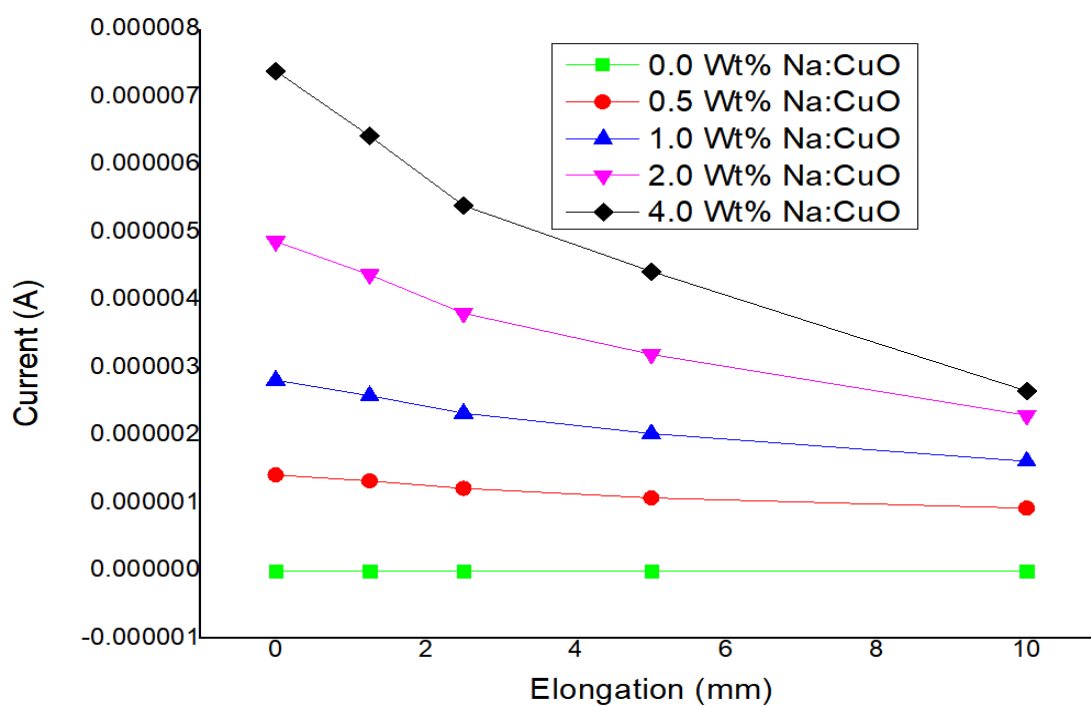


Figure 6: Plot of Tensile Elongation vs Current Conductivity in Pristine and Na:CuO-doped PU Films.

Conclusion:

Na:CuO/PU nanocomposites were prepared using prepolymer method at various filler content. Polymer was synthesized from castor oil and FTIR studies revealed the successful formation of Urethane Linkages. XRD spectrum revealed the presence of Na:CuO nanofillers in prepared films with diffraction peaks at 2θ values of 35.58° and 38.75° . The study of morphological characteristics using SEM revealed uniform dispersion of the filler in the matrix with few agglomerates at 4wt% filler concentration. EDX analysis also supports the presence of urethane links and filler contents in the films. Electro-Mechanical testing reveals the applicability of the prepared films for sensor applications by exhibiting the property of proportional change in conductivity values with reverence to tensile elongation. Also it was observed that films with 4wt% filler concentration revealed sudden decline in conductivity values after tensile stretching beyond 3.0 Millimetre. Films with filler 2 wt% and below show promising linear decrease in conductivity values relative to tensile elongation which could lead to applications in motion/joint sensing products.

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