PREPARATION OF MIXED METAL OXIDE (ZN AND CUO) NANOPARTICLES DOPED POLYMER (PMMA) COMPOSITE FILMS USING SOLUTION CAST METHOD

Abstract

We developed mixed zinc-copper oxide, pure copper oxide, and pure zinc oxide (ZnO, CuO) polymer composite films in five different ratios by Sol-Gel: 2-10gm, 4-10gm, 6-10gm, 8-10gm, and 10-10gm. We created pure PMMA and made weight-percentage doped PMMA films with pure ZnO, pure CuO, and mixed Zinc-Copper oxide. Composite films made of prepared materials and PMMA Using the solution-casting method, films up to 100 nm thickness.

Keywords: Zinc Oxide Nanoparticles, of Zinc-Copper Oxide, Copper Oxide Nanoparticles, Sol-Gel Technique.

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I. INTRODUCTION

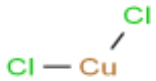
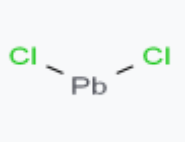
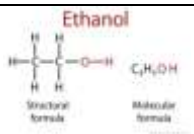
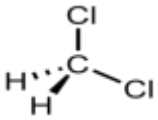
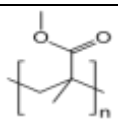
By the middle of the twenty-first century, In the future, nanotechnology will probably have a major impact in terms of economy and society. Science and innovation research in this field ensures advancements in fields like energy, biotechnology, information technology, materials and assembly, nano gadgets, medicine and medical services, and national security. There is a general consensus that nanotechnology will lead the next technological revolution. [1-3] Polymer nano composites are special because they are lightweight, highly flexible, and skillfully made at low cost and temperature. In many areas of life, polymers are replacing metals and are of great interest to society. They can also be further modified for use in modern applications. In industries like packaging, construction, and medical applications, they are preferred over conventional materials. In order to process polymeric materials, pressure and heat must be applied.[1] A material is essentially a combination of at least two different materials, each of which has unique properties. Typically, the term "composite" refers to materials that are created mechanically by joining at least two distinct materials. Although the polymer has amazing optical qualities, it is poorly scratch resistant. The rigid polymer chains give it a tolerable level of dimensional stability. [7] It is resistant to the elements and stable against corrosive and soluble bases. It is attacked by a few natural solvents and has a greater effect strength than polystyrene or glass. It has the most simple, straightforward optical properties of any thermoplastic that is commercially available.[8]

PMMA is a transparent plastic that transmits light nearly perfectly (92%), making it suitable to serve as a conduit for light. Dichloromethane, a chemical compound, PMMA dissolvent is considered because it has the highest soluble limit for PMMA, the best evaporation rates, and the lowest chemical hazard due to its lower viscosity than alternative solvents. [4-6,9] Due to their numerous uses in superconductors, optical, electrical, catalytic, photocatalytic degradation, gas sensors, and biosensors, oxide (CuO) nanoparticles are widely used.[10] A number of composite films containing potassium chromate,[10] potassium permanganate (KMnO4), [11] and tin chloride (SnCl2), [12] doped poly (methylmethacrylate) (PMMA) have been synthesized by the authors previously. The authors have stated in all of these publications that all dopant material significantly alters the optical parameters. We were intrigued by the results and inspired to look further, which is why we reported here. In this article, we describe how to make ZnO and CuO nanoparticles and ZnCuO/PMMA nanocomposite films.

II. MATERIALS

During the entire research work the chemicals used are listed in the below table:

S. No.	Name of Chemical	Chemical Formula	Structure	Firm	Physical Properties
1	Zinc Chloride	$ZnCl_2$		Merck Life Science Private Limited, Mumbai	Soluble in ethanol, glycerol and acetone Density-2.907 g/cm^3 White crystalline solid

2	Copper (II) Chloride	$CuCl_2$		Merch Specialties Private Limited, Mumbai	Blue-green solid (dehydrate) Soluble in methanol ,ethanol, Acetone. Density- 2.51g/cm^3 (dehydrate)
3	Lead(II)Chloride Anhydrous pure 98%	$PbCl_2$		Loba Chemie Pvt. Ltd., Mumbai	white odorless solid Slightly Soluble in dilute HCl, ammonia; Density- 5.85 g/cm^3
4	Hydrochloric Acid Pure 35%	HCl	H-Cl	Himedia Laboratories	Liquid, colourless-light yellow Soluble in cold water, hot water.
5	Ethyl Alcohol	C_2H_5OH		Himedia Laboratories	Colorless liquid easily soluble in water and is itself a good solvent.
6	Dichloromethane purity of 99.8%	CH_2Cl_2		Merch Specialties Private Limited, Mumbai	Colorless liquid Miscible in ethyl Acetate, Alcohol, Hexanes, Benzene, CCl_4, diethyl Ether, $CHCl_3$.
7	Poly (methylmethacrylate)	$(C_5O_2H_8)_n$		M/s Gadara Chemicals, Bharuch.	Density- 1.18 g/cm^3

1. **Synthesis of Zinc Oxide Nanoparticles using Solution Casting:** Zinc chloride (ZnCl2) and sodium hydroxide (NaOH) were the two initial components for the production of zinc oxide particles. At 50 degrees Celsius, we stirred 5g of NaOH in distilled water using a magnetic stirrer. We then filled a beaker with distilled water, added 8.5 gm of zinc chloride, and stirred it once more using a different magnetic stirrer. NaOH solution was being stirred while ZnCl2 solution was being continuously and dropwise added. An aqueous alkaline solution that has been treated with ZnCl2 will precipitate ZnO right away, turning the solution from transparent to white. Precipitated washed five times with distilled water in order to completely remove residues from the suspension. After drying, the final precipitates were produced.

2. **Synthesis of Copper Oxide Nanoparticles using Solution Casting:** Sodium and copper chloride (CuCl2) the two initial ingredients for the production of copper oxide nanoparticles were sodium hydroxide (NaOH). We used a 1.5.gm of NaOH in 40 ml of ethanol and stirred it at room temperature in a beaker being stirred by a magnet. Afterwards, we used a beaker to hold 1 g of copper chloride in ethanol used a different

magnetic stirrer to stir it. added NaOH solution Drop by drop, continuously, and allowed to in CuCl2 solution thirty minutes of stirring. The NaOH solution was dropped reaction happens in a copper chloride solution, and Dark blue turns to black in colour. Paper filters are used for sample was permitted after the gel was filtered and washed with water and dry at room temperature.

3. **Synthesis of Zinc-Copper Oxide Nano Material Using Sol-Gel Technique in Different Composition:** The precursors Copper Chloride $CuCl_2$ and Zinc Chloride $ZnCl_2$ were made to react with hydrochloric acid and ethanol in presence of dry ether at 60°C to produce the mixed metal as explained in the reaction stated below: -

$$CuCl_2+ZnCl_2+2HCl+C_2H_5OH \xrightarrow[\text{Dry ether or Hcl}]{\text{ZnCl2(anhy.)}} [\text{Cu-O-Zn}] + 3C_2H_6\uparrow + 6Cl\uparrow \quad \text{---------- (1)}$$

Anhydrous $ZnCl_2$ acts as a basic reactia in the above reaction and is the Lucas reagent. 1-Copper, 2-Zinc superoxide is the IUPAC name of [Cu-O-Zn]. In subsequent sections, we explain how MMO or mixed metal oxides can be prepared for different ratios of precursor salts, such as 2:5 and 4:5.

4. **Synthesis of Zinc-Copper Oxide in Ratio of 2:5:** For above preparation we took 10gm copper chloride and 4gm zinc chloride to obtain Zn-CuO ratio 2:5. This will be referred as sample COZ1. The reaction between 20 ml of hydrochloric acid and the white-colored zinc chloride anhydrous powder and the blue-colored copper chloride powder was allowed to proceed in the beaker over the magnetic stirrer for nearly an hour.

After that, we added ethanol (w/v 99%) to the solution, which was initially yellowish with a hint of blue. We then allowed the mixture to stir for an additional four hours at room temperature until it transformed into a denser gel that was blue in color. The precursors and ethanol's OH functional group interact in this process. Figure 1 illustrates the rapid formation of a rigid gel form of zinc-copper oxide after stirring was stopped and the solution was allowed to evaporate at room temperature. A reaction occurred within a few minutes of this time. The dry powder is then produced by heating this gel to 60°C in an oven for characterization purposes. This prepared MMO gels will be referred to as COZ1.

Figure 1: Picture of Xerogels of Zn-CuO in ratio 2:5

5. **Synthesis of Zinc-Copper Oxide in 4:5 Ratios:** For synthesis of zinc-copper oxide in ratio 4:5 we adopted the same procedure as explained in 2 except that the amount of precursor were taken in the following ratio ; we took 10gm of copper chloride and 8gm of zinc chloride to react this with hydrochloric acid and later ethanol. This prepared Zn-CuO gels will be referred to as COZ2.

   One can see the difference in colour, texture and homogeneity on change of composition.

Figure 2: Pictures of xerogels of zinc-copper oxide in 4:5 ratios

III. DEVELOPMENT OF PURE PMMA POLYMER FILM

The thin film of pure PMMA is prepared using solution cast method. The procedure undertaken is explained below:

We took a calculated fixed amount of granular PMMA and dissolved it in solution of dichloromethane and ethanol using a ultrasonicator. The process of stirring in ultrasonicator continued for 6 hours at room temperature to assure the uniform dispersion of polymeric chains to provide homogeneous solution. After this we pour the solution into flat bottom glass Petri dish of 9cm diameter. The petri dish is made to be placed over another petri dish of larger diameter containing mercury so that the smaller Petri dish flouts over mercury providing uniform leveling for preparation of film. We leave this for 24 hours so that the solvent disappears slowly at pervasive temperatures at atmospheric pressure. And the sample is obtained in form of dry film of 120 micro meters PMMA. This dried film is taken out from petri dish using tweeze clamp.

Figure 3: Film of Pure PMMA Polymers

Development of Zinc-Copper Oxide doped PMMA Composites

1. **Development of Zinc-Copper Oxide of ratio in 2:5 Doped PMMA Films:** As a solvent, spirit is used to dissolve a predetermined quantity of paper PMMA in 20 ml of dichloromethane. To ensure the homogenous dispersion of polymer particles without concentricity throughout the solvent to obtain a homogeneous solution, the molten PMMA is stirred uniformly on an ultra sonicator for 6 hours. While being stirred at room temperature, the solution. After that we took this solution in a 100ml beaker and added (.1) gm. of COZ1 and allowed this on a magnetic stirrer for overnight. The solvent was then allowed to slowly evaporate for almost 24 hours at ambient temperature and pressure after being poured into a glass Petri dish with a flat bottom and floating over mercury. Tweezers clamps were then used to peel the dried samples off. Below is a sample film with a 120 micrometre PCOZ1 thickness.

Figure 4: (a) Developed Zn-CuO-PMMA for 2:5 ratio solution (b) Zn-CuO of 2:5 doped PMMA Polymer Composite Film

2. **Development of Zinc-Copper Oxide of Ratio in 4:5 Doped PMMA Films:** For synthesis of Zn-CuO doped PMMA composite film for another composition we adopted the same procedure as explained in 2.3.1, the developed MMO doped PMMA composite film in figure 5.

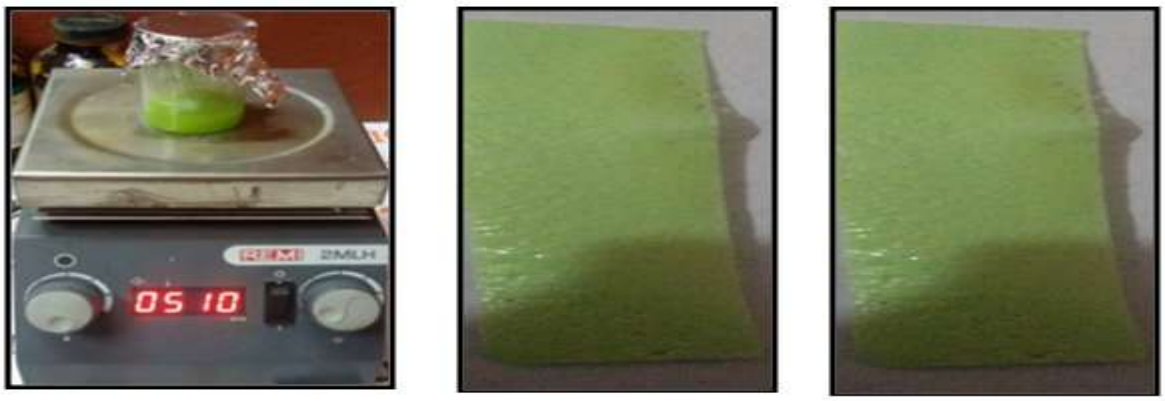


Figure 5: (a) Developed Zn-CuO-PMMA for 4:5 solutions (b) Zn-CuO of 4:5 Doped PMMA composite Film

IV. SYNTHESIS OF LEAD-COPPER OXIDE NANO COMPOUND USING SOL-GEL TECHNIQUE

For this purpose we used the respective metals and precursor; reacted them with hydrochloric acid and ethyl alcohol to obtain the respective mixed metal oxides. The preparation of each mixed metal oxide is explained below: -

The precursor salt ratios used to prepare these mixed metal oxides were 2:5 and 4:5. The sol-gel method is a way to turn small molecules into gel from solid materials. The process is used to create MO, MMO, and M-O-M'. It can be made by partially summarizing and hydrolyzing precursors like metal chlorides, metal alkoxides, and metal nitrates. the further blending of sol particles with a gel substance. The solids in the gel enclose the solvent, making it a dysphasic substance. Additionally, we have used X-ray diffraction, Raman spectroscopy, FTIR spectroscopy, and FESEM technique to characterize these structural properties.

1. **Synthesis of Lead-Copper Oxide in Ratio of 2:5**: For this Synthesis we took the metal chlorides starting precursor reacted them with hydrochloric acid and ethanol to obtain the respective metal-oxide-metal. The preparation of metal-oxide-metal is explained below: -

$$PbCl_2 + CuCl_2 + 2HCl + 2C_2H_5OH \xrightarrow[Dry\ et\square er\ or\ HCl]{ZnCl2(an\square y.)} [Pb\text{-}O\text{-}Cu] + 3C_2H_6\uparrow + 6Cl\uparrow$$

These mixed metal oxides or metal-oxide-metal compounds have been created in a 2:5 precursor salt ratio. We used 4 grammes of lead chloride and 10 grammes of copper chloride to create lead-copper oxide in the 2:1 ratio, one of the many different ratios possible.

After this lead chloride and copper chloride made them to react with 20ml of hydrochloric acid and kept it over magnetic stirrer for 1 hour, after this we added ethyl alcohol in to this solution and kept stirring it for four hour at room temperature during this time solution reacts with OH group. Within a few minutes, a reaction took place, followed by the quick formation of a rigid gel. Then, we warm up this solution to a temperature of 60 degrees Celsius. so that the solvents evaporate, leaving behind a gel of lead-copper oxide, or metal-oxide-metal, that is green in colour. And after this gel dried in a 60° oven, its solvent changed into a hydrous form. Because M-O-M's properties change at temperatures above 60 degrees, we were unable to calcine them, and their colour changed from green to black.

Figure 6: Picture of Prepared [Pb-CuO]

2. **Synthesis of Lead-Copper Oxide in Ratio of 4:5:** For this Synthesis, we used metal chlorides as the initial precursor and then reacted them with ethanol and hydrochloric acid to produce the corresponding metal-oxide-metal. The following describes how metal-oxide-metal is made: -

These mixed/metal oxide compounds, also known as metal-oxide-metal compounds, were created in a 4:5 precursor salt ratio. We used 8 grammes of lead chloride and 10 grammes of copper chloride to create 1-copper, 2-lead superoxide in various ratios of the constituent metals, resulting in a lead-copper oxide ratio of 4:5.

Figure 7: Picture of prepared Pb-CuO

After this lead chloride and copper chloride made them to react with 20ml of hydrochloric acid and kept it over magnetic stirrer for 1 hour, after this we added ethyl alcohol in to this solution and kept stirring it for four hour at room temperature during this time solution reacts with OH group. Within a few minutes, a reaction took place, followed by the quick formation of a rigid gel. Then, we warm up this solution to a temperature of 60 degrees Celsius. so that the solvents evaporate, leaving the lead-copper oxide (also known as mixed metal oxide) in gel form and a green colour. And this gel dried in oven 60 degree temperature, then gel solvent changes in to hydrous form .we couldn't perform the calcinations process of M-O-M compound because higher than 60 degree above temperature its changes their properties and color became green to black.

V. DEVELOPMENT OF LEAD-COPPER OXIDE NANO COMPOUND DOPED PMMA COMPOSITES

1. **Synthesis of Lead-Copper Oxide of Ratio in 2:5 doped PMMA Films**: A predetermined quantity of PMMA is measured, and it is then broken down in dichloromethane with spirit acting as a solvent. To obtain a specious (homogeneous) solution, the diffluent (moulted) PMMA is stirred uniformly on a magnetic stirrer for 6 hours. This ensures that the polymer particles are dispersed throughout the solvent without concentricity. While being stirred at room temperature, the solution. After that, we added lead-copper oxide, a product of the sol-gel process, in a 2:5 ratio to (.1) gm of material, and stirred it for the remainder of the night. The solvent was then allowed to slowly disappear at pervasive temperature under atmospheric pressure for almost twenty four hours after being poured into a glass flat-bottom Petri dish that was floated over mercury for 24 hours. Tweezers clamps were then used to peel the dried samples off. The

solution casting method was used to create the pure PMMA films, and the same steps were followed.

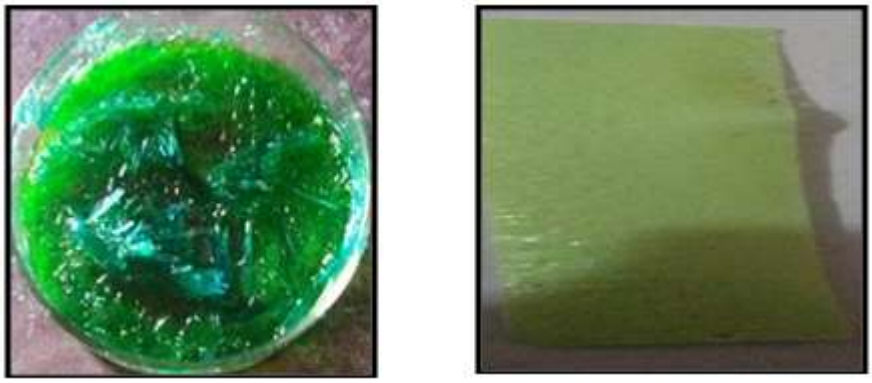


Figure 8: Picture of Prepared Pb-CuO of 2:5 Ratio Film

2. **Synthesis of Lead-Copper Oxide of ratio in 4:5 doped PMMA Films:** A foresee amount of paplour PMMA is measured and decomposed in dichloromethane with sprit which works as a solvent. The diffluent (molted) PMMA is stirred uniformly on a magnetic stirrer for 6 hrs to assure the dispersion of polymer particles without concentricity throughout the solvent to get a specious (homogeneous) solution. The solution was stirred at room temperature. After that we have added lead-copper oxide which is obtained from sol-gel process, in the ratios of 4:5 in (.1) gm. quantity and stirred for overnight. Then poured into a glass flat bottom Petri dish floated over mercury for 24 hours, and the solvent was allowed to disappear slowly at pervasive temperature under atmospheric pressure for almost twenty four hours. The dried samples were then peeled off by tweezers clamp. The pure PMMA films were made by solution casting method by following the same procedure.

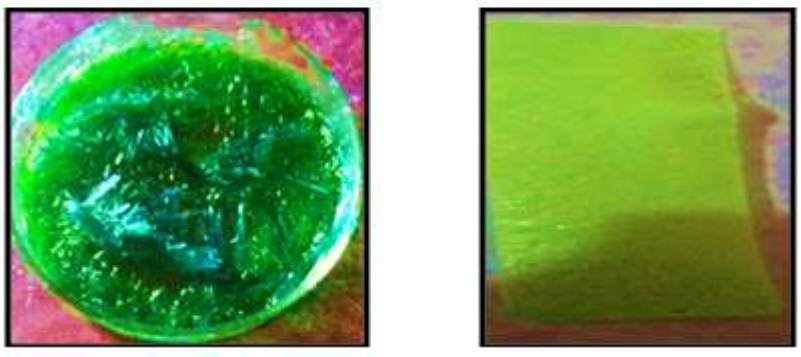


Figure 9: Picture of Prepared Pb-CuO of 4:5 Ratio Films

In the Malviya National Institute of Technology, we used a "X-ray" diffractometer (PANalytical unit using software X'Pert°Pro3) equipped "with Cu-K radiation" of wavelength = "1.5406A°" at an accelerating voltage of 30 kV to study the synthesized Zn-Cu oxide and Pb-Cu oxide nanoparticles and their doped PMMA films. In the material research Centre (MNIT, Jaipur), the surface structure of the composite samples was

examined using an S-3700N FESEM field emission scanning electron microscope. The material research Centre (MNIT, Jaipur) used an FTIR Perkin Elmer Spectrum Version 10.4.00 FTIR Spectrophotometer to analyze the functional group composition of our powdered samples and prepared films in the range 400-4000 cm-1. A confocal micro-Raman spectrometer called the STR5050 (400 nm–3000 nm) was used to measure the samples' Raman spectra. In the material research Centre (MNIT, Jaipur), a diode pumped solid state (DPSS) laser with a wavelength of 532 nm was used as an excitation source. Fluorescence emission spectroscopy was used in the material research Centre (MNIT, Jaipur) to obtain the FL spectra.

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