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Synthesis of Ceramics & Its Application in **Bio-Plasticizer**

Pranjali T. Maskar^{*1}, Sanjay Bapurao Ghorpade² and Praful Tekale³

*1Assistant Professor, Department of Chemistry, B.K. Birla College of Arts, Science and Commerce (Autonomous), Kalyan-421301, Maharashtra, India. pranjalimaskar@gmail.com

²Research Scholar, Department of Chemistry, B.K. Birla College of Arts, Science and Commerce (Autonomous), Kalyan-421301, Maharashtra, India. sghorpade@mes.ac.in

³Assistant Professor, Department of Chemistry, Guru Nanak Khalsa College of Arts, Science and Commerce (Autonomous), Matunga (Mumbai), Maharashtra, India. Praful.tekale@gnkhalsa.edu.in

Abstract: Mechanical, chemical properties and thermal degradation of natural rubber like compounds containing bio plasticizer were studied to evaluate its suitability as plasticizer. Castor oil was used as a reference plasticizer. Higher the free fatty acid higher is the oxidation number of plasticizers. Adverse effect of fatty acid on bio-plasticizer indicates loss of it during processing. In order to prevent this problem metal ceramics were added in the bio-plasticizer. Saponification number, acid number of plasticizers lowered and flash point of plasticizer considerably enhanced. and viscosity does not alter due to the addition of metal ceramics of magnesium, copper and iron in bio- plasticizer like castor oil. Combustion method was very suitable method for synthesis of metal ceramics in which citric acid its self-act as a fuel in combustion process and nitrate salt acts as a oxidising agent. The ceramic powder obtained by this technique generally has the highest degree of phase purity with improved powder characteristics such as narrow distribution of particles, higher surface area and better sinter ability. The resultant metal ceramic powder having required phase purity and considerable amount of carbonaceous residue, depending upon the nature and amount of the fuel used in the process.

Key words: Metal salts of iron and magnesium, citric acid, water. Copper nitrate heating mantle.

I. INTRODUCTION

By using Zn, Al(NO3)3·9H2O, HNO3, C6H8O7·H2O, CH4N2O as raw materials, Al doped ZnO (AZO) nanoparticles were successfully prepared by a novel sol-gel combustion method. Characterization done by TG-DTA, XRD, EDS, FESEM and Archimedes' method. At PH 4, and temperature 600 oc Al doped ZnO nanoparticles synthesized [1]. For the synthesis of Nano crystalline Hydroxyapatite (HAP) powder from calcium nitrate, ammonium hydrogen phosphate and citric acid, the citric acid sol-gel combustion method has been used.

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By the citric acid sol-gel combustion method, Nano crystalline at a low calcination temperature HAP powder has been synthesized at 750oC [2].

The novel silicate bio ceramic larnite was prepared by combustion technique and it was calcinated at moderate temperature. Thus, powder was prepared at temperature ranging from 400 to 800oc. Preparation and and antibacterial activity of calcium silicate was studied [3]. The radio luminescence of the transparent ceramics was similar to that for calcined powders, except higher in intensity [4]. In the preparation of ceramic powder by sol-gel method, starch was used as a polymer sing agent. It has been observed that Starch was a highly energetic fuel that provides energy during combustion and Starch helped to control particle size of the powders and prevents agglomeration [5]. With the direct reaction of silicon powders with carbon black, Nano crystalline SiC ceramic powders were synthesized. Investigation of effect of reaction of reaction temperature on the phase product done. Average particle size of SiC was 48.56nm. Shape of particle was spherical and sintering temperature was 1850oC.It has been observed that relative density of nanoceramics was up to 99.2%.and a high flexural strength of 580 MPa, which exhibits better sintering activity of synthesized SiC nano powders [6]. CoFe2O4 nanoparticles were prepared by sol-gel auto combustion method. Different fuels were used in that preparation. Different properties of CoFe2O4 nanoparticles were studied. Smaller particle size was achieved by using urea. It was observed that nature of particle was supramagnetic. Improved magnetic properties was achived due to ethylene glycol as fuel [7]. In the gel combustion method, template of lead zircon ate titanate used. Phase analysis was done by XRD.SEM analysis proved that excellent mixture development in the composite powder. It was also observed that magnetic and dielectric behaviors of the ceramic composites vary with the ratio of the two phases [8]. Magnesium aluminate (MgAl2O4) ceramic material was synthesized by gel combustion method. Nano crystalline spinel type ceramic was prepared by using combustion method. The morphology, structural, microstructural, analysis was done by different techniques like XRD, FTIR, surface area analyzer (BET) and impedance spectroscopy [9]. Oxidation process acted as a flame retardant material as well as excellent heat stabilizer [10]. By incorporating micro-sized or nano-sized inorganic fillers such as Al2O3, SiO2 or TiO2 in to solid polymer (Poly (ethylene oxide) (PEO)-based composite polymer), its ionic conductivity was increased. Due to ceramic filler (Al2O3), ionic conductivity of polymer increased. Glass transition temperature of plasticizer and filler-added polymer electrolyte samples seen in the DSC thermo grams [11]. Alumina filler was incorporated with excess metallic silver nanoparticles, was added in the chitosan:Agnt based polymer. It has been found that remarkable enhanced surface plasmonic resonance (SPR) peaks at 420 nm for samples containing various amounts of alumina (Al2O3) were attributed to the increase in the amount of silver nanoparticles [12]. Polylactic acid (PLA), an aliphatic polyester was obtained from renewable sources and applied for various industrial uses. It was observed that change in the thermal conductivity of 30% alumina filled PLA after a hydrophobic surface modification was applied to the filler. The improvement in the interaction between the modified alumina and PLA matrix was investigated by examining the morphology micrograph obtained by field emission scanning electron microscopy [13].



Fig 1: a. Diffusion-controlled, b. Evaporation-controlled plasticizer loss from polymers to a gas phase, c. Image of a nitrile butadiene rubber (NBR) sample aged at 90 °C for 48 h ref- [14].

There was tremendous loss of polymer during the storage and transport. Loss of plasticizer means the degradation of plasticized polymer product. Loss of polymer was due to poorer mechanical properties and eventual contamination of the surrounding environment. Plasticizers were migrated from polymer to the surrounding gas phase., Plasticizer, was not chemically attached to polymer chains, in certain conditions leave the polymer through migration, evaporation or extraction by liquids. During service, this loss may be problematic; it leads to unwanted changes in the material properties e.g., poorer mechanical properties) and eventual contamination of the surrounding medium [14].

Flexible plastic was the requirement of the automotive industry, medical and consumer products. Technical issues and leaching, migration, evaporation and degradation issues were observed during the applications. In order to reduce evaporation and degradation of plasticizers, the development of fire-retardant plasticizers and novel plasticizers for use in biodegradable plastics were included.[15]

Polyvinyl chloride was prepared from mixture of dibasic acids and individuals alcohols has carbon number 4 to 10. Dieters were a starting material for pvc. By ozonolysis monobasic acids obtained and these acids easily removed by distillation. After removal of monobasic acid by distillation leaved mixed dibasic acids that was esterified to yield diester plasticizers known as azela-brassylate [16]. Plasticized polymer materials were extensively used in all spheres of human life It has been observed that use of propylene adipate modified with cyclohexane carboxylic acid provides a plasticizing efficiency as high as dioctyl phthalate (DOP) while having a reduced migration and use of calcium adipate nano quantities in the production of propylene glycol adipate increased the yield of the desired ester and improved the physical and mechanical properties of PVC plastic.

Structure of composition	Mass parts
PVC	100
Plasticizer	70
Epoxidized Soybean oil	5
Stabilizer	2
Calcium Adipate	0.4

Table II: Physical	and c	chemical	properties	of synt	hesized
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Compound	Acid number	Flash	Pour point
	mgKOH/g	point °c	°c
PPA/DCG	0.30	245	-43

It has been observed that the introduction of nano quantities of calcium adipate improved some of the physical and mechanical properties of PVC plastic, namely the thermal stability index [17]. Natural or biodegradable plasticizers with low toxicity and good compatibility with several plastics, resins, rubber and elastomers were superior applications than conventional plasticizers. such as phthalates and other synthetic conventional plasticizers [18]. In order to increase the physical and mechanical properties of polyvinyl chloride some additives were added in it. Different additives or fillers mixed with base polymer. Plasticizing additives like diisooctyl phthalate (DIOP) (40 phr) and epoxidized soybean oil (2-3 phr) with general plasticizer (50-80 phr) incorporated in to plasticizer for the preparation of Cable compound and shoe compound[19].Vinyl resin emulsion or dispersion such as polyvinyl acetate emulsion were assumed as a fully polymerized emulsion in which flame proof plasticizers such as organic liquid like tricresyl phosphate, the polyvinyl acetate and tricresyl phosphate emulsified .In emulsion fire -proof metallic oxide or fillers like antimony trioxide and manganese carbonate and pigments such as chromium oxide, and iron oxide were added[20].Metallic nano fillers were added in natural rubber. Copper doped nano filler in rubber shown excellent mechanical properties. By using coprecipitation method differently doped ferrites were fabricated. Mechanical studies of the composite such as hardness, specific gravity, tear and tensile strength done.Nickel ferrite and doped Nickel ferrites blended composite were compounded. Dispersion of metallic filler over the natural rubber matrix critically enhances the mechanical properties of composites. The prepared nano fillers were characterized via SEM, FTIR and XRD and confirms the formation of spinel structure. It was found that all the mechanical properties are excellent for copper doped samples and these samples can be efficiently used for shielding purposes [21]. There was in carporation of micro sized aluminium powder with different ratio on the matrix of the elastomer.Incarporation based on quality of waste rubber.It has been observed that designed composite was used for construction material.



Fig 2. A. Recycled rubber particles. B. Aluminium chips before grinding Material used in preparing the composite mixture



a ball mill Fig 3. Aluminium powder preparation [ref-22]



(c) blanking tool(d) Specimen tensile testFig 4 Process of specimen preparation [ref-22]



Fig 5. Tensile strength of compound[ref-22]



It has been observed that tensile strength and hardens of the rubber enhanced due to incorporation of the aluminium particles in it [22]. Nano titanium dioxide/silica fume waste in the presence of silane coupling agent and polyethylene glycol as a dispersing agent was incorporated in a blend of SBR/NBR (50/50). It has been observed that nano titanium dioxide and silica interact chemically with the rubber by the formation of Ti– O–Si between nano titanium and the silane coupling agent and Si–O–Si between the silica fume and silane coupling agent [23]. Ferroelectric ceramic materials like barium titanate (BaTiO3) and lead titanate (PbTiO3) were prepared by solid-state reaction. Calcination temperature was 11000c for 2 hrs. Ceramic was incorporated in the rubber. Mechanical, morphological, and dielectric properties of natural rubber (NR) vulcanizate was studied. It was investigated that BaTiO3 composites showed finer and better distribution of the particles in the rubber matrix than that of the PbTiO3 composites. It was also observed that incorporation of ceramic powders in rubber matrix and the presence of epoxirane rings in ENR molecules caused faster curing reaction, and higher delta torque but lower elongation at break [24].

II. OBJECTIVES

Ceramics prepared by various chemical methods. One of the methods is combustion method in which fine, amorphous, uniform ceramic powder is synthesized. High surface area, better sinter ability, the highest degree of phase purity with improved powder characteristics like narrow distribution of particles. These are the significance of the combustion method.

Steps of combustion method:

- 1. To prepare the ceramic by combustion method.
- 2. To investigate the effect of metallic ceramic on the plasticizer.
- 3. To investigate the factors which influence the sustainability of bio- plasticizer

To prevent the loss of bio-plasticizer at high temperature by incorporation of ceramic in it.

III. EXPERIMENTAL PROCEDURE

Development of liquid precursor of metallic salt:

In this step appropriate quantity of nitrate salt of copper and salts of iron, magnesium was mixed with aqueous media. Solvent citric acid acted as fuel and nitrate salt are oxidants. Nitrates fulfill the requirement of oxidant by providing the oxygen for burning of the fuel. Fuel maintains the compositional homogeneity among constituents. The transparent aqueous solution containing mixture of salt of copper, salt of iron and salt of magnesium converted to a viscous liquid by thermal dehydration at about 70-110 °C. In order to prepare transparent viscous gel without any phase separation or precipitation, the nature of the fuel, its amount and pH of the starting solution are some of the important process parameters. Gel precursor was prepared on heating mantle with continuous heat supply. The basic idea of the first step is to maintain an intimate blending between fuel and an oxidant.

Combustion of precursor

Combustion reaction triggers at about temperature 150-250 °C at which precursor was heated up to its melting temperature.

The reaction was exothermic with decomposition of the fueloxidant precursor with association of evolution of gases and formation of ceramic powder.







Fig 8. Images of the ceramics



Fig 9. Images of the bio- plasticizer incorporation with ceramic powder A. Bio-plasticizer, B. Bio-plasticizer with ceramics

IV. OBSERVATIONS

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Sr.	Flash point of	Flash point of plasticizer+
no.	plasticizers (^O C)	metallic ceramic (^O C)
1	229	235
2	229	235
3	230	235
4	230	235
5	230	235
6	230	236
7	230	236

Table III: Flash point of plasticizers with ceramic

Table IV: Stability of plasticizer

G		Ageing	Flash point of
Sr.	Stat: 1:tes	Flash point of	plasticizer + metallic
no.	Stability	plasticizers g	ceramic (^O C)
1	1 st hour	229	235
2	2 nd hour	229	235
3	3 rd hour	230	235
4	4 th hour	230	235
5	5 th hour	230	235
6	7 th hour	230	236
7	7 th hour	230	236







Fig 11. Flash point of bio plasticizer Vs Flash point of plasticizer+ ceramic

Table V: Viscosity of bio plasticizer			
		Viscosity of	bio plasticizer
Temp in	Viscosity of	ceramic with	Ceramic with
°c	bio	plasticizer	plasticizer
	plasticizer	(blend -1)	(blend -2)
30	1450	1455	1455
40	1255	1256	1256
50	875	877	877
60	480	482	482
70	378	383	383
80	338	340	340
90	80	83	83





Table VI: Acid value of plasticizer

Temperature	Acid value of plasticizer	Acid value of ceramic + plasticizer
30	0.39	0.22
40	0.38	0.22
50	0.38	0.22
60	0.38	0.22
70	0.38	0.22
80	0.39	0.21
90	0.39	0.21

Table VII: Acid value of ceramic + plasticizer

Temp.30 ^o C	Acid value of plasticizer	Acid value of ceramic + plasticizer
1 st hour	0.39	0.22
2 nd hour	0.38	0.22
3 rd hour	0.38	0.22
4 th hour	0.38	0.22
6 th hour	0.38	0.22
7 th hour	0.39	0.21
8 th hour	0.39	0.21



Fig 13. Temperature Vs Acid value of bio plasticizer



Fig 14. Temperature Vs Acid value of bio plasticizer

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Temperature ^o C	Saponification value of bio plasticizer	Saponification value of ceramic + bio plasticizer
30	177.5	95.5
40	1768	96.5
50	177.4	95.5
60	176.6	96.5
70	177.6	95.6
80	177.8	96.5
90	177.5	96.5

Table IX: Saponification value of ceramic + bio plasticizer

Temperature	Saponification	Saponification value
30°C	value of bio	of ceramic + bio
	plasticizer	plasticizer
1 st hour	177.5	95.5
2 nd hour	1768	96.5
3 rd hour	177.4	95.5
4 th hour	176.6	96.5
6 th hour	177.6	95.6
7 th hour	177.8	96.5
8 th hour	177.5	96.5



Fig 15.Temperature Vs Saponification value



Fig 16. Temperature Vs Saponification value



Fig 17. Characterization by stereomicroscope 100X



Fig 18. Characterization by stereomicroscope 150X

V. RESULTS AND DISCUSSION

It has been observed that viscosity value of bio-plasticizer does not alter due to incorporation of ceramic in it. Acid number and saponification number of plasticizers significantly reduces due to addition of ceramic powder. Flash point of plasticizer increases with addition of ceramic powder.

- Homogeneous, amorphous of very fine particles prepared as a ceramic powder.
- The pure, fine powders of oxide of copper, iron and magnesium develope at a lower calcination's temperature by the combustion method.
- High surface area and stable surface of the product obtained is the advantage of combustion method
- Acid value of plasticizer with ceramic decreased by 55 % than that of the plasticizer.
- Saponification value of plasticizer with ceramic decreased by 54 % than that of the plasticizer.
- Flash point of plasticizer increased 2 % after incorporation of ceramic powder.
- Decreasing of acid value indicates no loss of plasticizer at elevated temperature
- Less acid value suggests that oxidation of bio-plasticizer is low and it can be use as lubricant.
- Loss of plasticizer at high temperature reduces

VI. CONCLUSION

It was observed that there was huge loss of plasticizer during the processing. In order to prevent loss of castor oil as a bio-plasticizer during processing ceramic was incorporated in it. Lowered acid number and saponification number indicates that less oxidation and esterification values of castor oil. Due to poor heat resistance, brittle at low temperature, poor wear resistance and easy aging, cost of oil was enhanced. Due to addition of ceramic in castor oil all above parameters may improve and cost of processing of bio- plasticizer may reduce.

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