2. REVIEW OF LITERATURE

Polymers in the form of elastomers and plastics have improved the quality of life over the last five decades. This materials are extremely versatile and have large number of applications, but dominate in packaging, followed by building and construction, automotive, electrical and electronic sectors, and other sectors such as medical and leisure.\textsuperscript{1} Production of plastic materials started on an industrial scale in the 1940s and 1950s. In the last 15 years the global annual production of plastics has doubled, reaching 245 million tons in 2008.\textsuperscript{1}

The ever growing consumer demand for both commercial and domestic plastic materials is mainly due to their ease in availability, affordable cost, user friendly nature and wide range of colored and desired shapes. However these plastics may take years to degrade and thus have both environmental and health hazards. Environmental factors such as light, heat, moisture, chemical and biological processes may bring about physical and chemical changes in the polymers causing bond breaking and structural changes.\textsuperscript{2,3} Such polymer degradation causes cracking, erosion, discoloration and delaminating etc.\textsuperscript{4} In order to enhance the quality of the commercial plastics many chemicals, as additives of various types are added to obtain the desired properties. These include stabilizers, fillers, plasticizers, pigments, antioxidants and flame retardants etc.\textsuperscript{5,6} The common use of various inorganic elements such as Al, As, Ba, Br, Ca, Cd, Co, Cr, Cu, Fe, Hg, Ni, Pb, Sb, Sn, Se, Ti and Zn etc., as these additives in plastics are also of concern from human exposure and pollution point of view as many of these elements are perilous for human health. Many adverse effects can be caused by the materials and different additives causing contamination and breakdown of the products that may result in harmful effects. To ensure safety and to validate that the polymeric materials will not critically
change with its short or long term usage, it is mandatory that these new and degraded plastic materials should be analyzed for their metal contents from health safety and environmental impact point of view.

At 17th February 2011, the European Commission announced a ban on use of six substances which is to be effective within three to five years, unless an authorization has been granted to individual companies for their use.\textsuperscript{7} Four of them are used in plastics, \textit{i.e.} the phthalate plasticizers Di-(2-ethylhexyl) phthalate (DEHP), Benzyl butyl phthalate (BBP) and Di-butyl phthalate (DBP) mainly used in PVC, and 4, 4’-methyleneedianiline (MDA) used as a curing agent for epoxy resins. Plastic products are made from plastic polymers in which additives are added to enable processing and/or to give certain desired properties for a specific application. They are made by polymerizing monomers into macromolecular chains.\textsuperscript{8} These monomers are almost exclusively derived from non-renewable crude oil. Approximately 4\% of world oil demand is used as raw materials for plastic production.\textsuperscript{9}

Other substances (besides monomers) are often needed for polymerization to occur, for instance initiators, catalysts, and depending on manufacturing process, solvents may also be used. The resulting plastic polymer can be blended with different additives, for instance plasticizers, flame retardants, heat stabilizers, antioxidants, light stabilizers, lubricants, acid scavengers, antimicrobial agents, anti-static agents, pigments, blowing agents and fillers, and is finally processed into a plastic product. There are many different plastic polymers and several thousand different additives, which results in an extremely large variation in chemical composition of plastic products.\textsuperscript{10} Plastic polymers are not particularly reactive and their large size limit transport across biological membranes.\textsuperscript{11} In the polymeric material, however, additives such as residual
monomers, oligomers, low molecular weight fragments, catalyst remnants, solvents used in polymerization and a wide range of additives can be present. Several of these are hazardous to human health and the environment, for instance carcinogenic, mutagenic, toxic for reproduction, sensitizing and hazardous to the human health. Since the non-polymeric compounds usually are of low molecular weight and are either weakly bonded or not bonded at all to the polymeric molecules, they, or their degradation products, can be released from the plastic product to air, water or other contact media (e.g. food). The residual monomer content depends on polymer type, polymerization technique and techniques for reducing residual monomer content. PVC is the plastic that requires by far the most additives. Of the world production of additives PVC alone accounts for 73% by volume, polypropylene and polyethylene account for 10 %, and styrene account for 5% . Many additives are hazardous for human health and the environment. Some are especially hazardous, for instance brominated flame retardants, some phthalate plasticizers mainly used to make PVC flexible; and lead heat stabilizers used to prevent degradation of PVC during processing. Several poly-brominated flame retardants are persistent, bio-accumulating and toxic, and are listed in the Stockholm Convention on Persistent Organic Pollutants (POPs). The lead compounds used as heat stabilizers are classified as toxic for reproduction (category 1A), very toxic to the aquatic environment with long lasting effects and may cause damage to organs. Release of hazardous substances from plastic products to air, extraction fluids, water, food, food simulants, saliva and sweat have been shown by chemical analysis. Examples of substances studied and released from various plastic products include phthalates, brominated flame retardants, bisphenol-A, bisphenol-A dimethacrylate, lead, tin and cadmium, formaldehyde and acetaldehyde,
nonylphenol,\textsuperscript{27,28} and other volatile organic carbons.\textsuperscript{29,30} Migration is generally favored if the polymer matrix is permeable; if the size of gaps between polymer molecules is larger than the size of migrant; if the migrant is small, has a similar solubility parameter as the polymer and is volatile; if the temperature is high; and if the surrounding medium is water for water soluble migrants, fat containing for hydrophobic migrant and acidic for metals.\textsuperscript{31,32} The degradation products formed during degradation will vary depending on polymer type.\textsuperscript{33} The type and quantity of degradation products formed may also be influenced by degradation mechanisms, presence of polymerization impurities, and surrounding factors, e.g. temperature and air.\textsuperscript{33,34} Polymers capable of de-polymerization by chain scission include polymethylmethacrylate, polytetrafluoroethylene, and polyoxymethylene, which can de-polymerize completely into their initial monomers. Also polystyrene, polyesters (e.g. PET and polycarbonate), nylon and polyurethanes can de-polymerize to some extent into their monomers.\textsuperscript{35-38}

The finished plastics are generally considered to be safe provided they are manufactured according to standard conditions using permitted chemicals recommended by national and international regulatory agencies and used properly.\textsuperscript{39-45} However, several workers have reported health disorders from use of plastics due to migration of un-reacted monomers, plasticizer, stabilizer, colorants, UV-absorbing materials, antioxidants, under the influence of physicochemical factors such as sunlight, temperature, type of solvent and pH of the stored commodity.\textsuperscript{46-52}

Due to the ever increasing use of the plastics, manufacturers are providing newer formulations and newer ingredients in plastics which should be analyzed. Toys are an integral part of children’s developmental processes. Children play with toys and learn about the world. Besides providing entertainment to children,
toys also serve as educational materials for them. Many items are manufactured to serve as toys, but any other items can also be used as toys depending upon children’s imagination and perception. The history of toys is as old as the history of human civilization. Toys can broadly be categorized as mechanical toys, electrical toys and soft toys.\textsuperscript{53} According to available figures, the global toy market presently is of the order of US$105.0 billion. USA is the world’s biggest importer of toys (imports worth US$35.0 billion) having a market share of approximately 30%. This is followed by Germany, which provides for 8\% of the world market (US$19.0 billion), succeeded by Hong Kong 13\% (US$14.0 billion), with Britain coming next at 7\% of the global market (US$8.0 billion) and France contributing 6\% (US$ 6.5 billion).\textsuperscript{54}

A toy may mean different things to children of different age groups and hence exposure pathways also differ accordingly. A child of below 3 years may handle a toy in a completely different manner from a child of 3-6 years age group. Chemical exposure to children, especially from toys, is an emerging concern. Children suck toys or sometimes chew them resulting in ingestion of harmful substances. Even short term exposure of such chemicals may cause severe and long term impacts on children’s health. Toy manufacturers add bright colours to toys to attract children. These only compound the problems as most of these colours are organo-metallic compounds and are added to toys during the last stage of manufacturing. Metals in materials and paints are loosely bound to the surface and can leach easily.

The concentrations of heavy metals such as Pb, Cd, Cr, etc in plastic baby toys, for instance, are regulated in many countries due to the obvious toxicity of these elements.\textsuperscript{55} It is well known that heavy metals are toxic, especially to young children; however, toys as well as other consumer products still contain these
metals. The chewing, licking and swallowing behavior of children is a common source of lead and cadmium exposure. 53, 56 Metals in toys and other materials are loosely bound to the surface and can leach easily to enter the food chain, to cause cancers, mental dysfunctions, energy, nervous system, kidney, lungs and other functions of organs to decline. 58-60 Lead poisoning from toys causes learning disabilities, kidney failure, anemia and irreversible brain damage in children. 61 Children and pregnant women are particularly susceptible to lead poisoning. 62-64 The digestive system of children absorbs up to 50% of the lead they ingest. 65 In fact, physicians and scientists agree that no level of lead in blood is safe or normal. 65 Cadmium compounds are used as stabilizers, colourants and pigments in PVC products. Cadmium exposure produces a wide variety of acute and chronic effects in humans, leading to a build-up of cadmium in the kidney that can cause kidney disease. 66 The International Agency for Research on Cancer (IARC) has classified cadmium as human carcinogen (group-1) on the basis of sufficient evidence in both humans and experimental animals. 67 Lead and cadmium are known poisons, being neurotoxins and nephrotoxins. Neurotoxins are agents that can damage the nervous system while nephrotoxins are agents that can damage the kidney respectively. 68 European studies have shown signs of cadmium induced kidney damage in the general population at urinary cadmium levels around 2-3 μg Cd/g creatinine. 69-70

Nickel in small amount is needed by the human body to produce red blood cells; however, in excessive amount, can become mildly toxic. Short-term over exposure to nickel is not known to cause any health problems, but long-term exposure can cause decreased body weight, heart and liver damage, and skin irritation.
Although zinc is an essential requirement for good health, excess zinc can be harmful. Excessive absorption of zinc suppresses copper and iron absorption.\textsuperscript{71} The free zinc ion is a powerful Lewis acid up to the point of being corrosive. Stomach acid contains hydrochloric acid, in which metallic zinc dissolves readily to give corrosive zinc chloride. This chloride can cause damage to the stomach lining due to the high solubility of the zinc ion in the acidic stomach.\textsuperscript{72} The U.S. Food and Drug Administration (FDA) has stated that zinc damages nerve receptors in the nose, which can cause anosmia.\textsuperscript{73}

Chromium metal and chromium (III) compounds are not usually considered health hazards; chromium is an essential trace mineral. Hexa-valent chromium is very toxic and mutagenic when inhaled, as publicized by the film ‘Erin Brockovich’, released in March, 2000. Cr (VI) has not been established as a carcinogen when in solution, though it may cause Allergic Contact Dermatitis (ACD). The lethal dose of poisonous chromium (VI) compounds is about one half teaspoon of material.

Cobalt is an element that can be both beneficial to an individual's health and detrimental to it. At its lowest levels, cobalt can be found in the chemical makeup of vitamin B12, which is necessary for optimum health, but if the body comes in contact with a high level of cobalt, it could ultimately be harmful to the heart and lungs.\textsuperscript{74}

Manganese overexposure is most frequently associated with manganism. Manganism is a biphasic disorder. In its early stages, an intoxicated person may experience depression, mood swings, compulsive behaviors, and psychosis. Early neurological symptoms give way to late-stage manganism, which resembles Parkinson's disease. Symptoms include weakness, monotone and slowed speech,
an expressionless face, tremor, forward-leaning gait, inability to walk backwards without falling, rigidity, and general problems with dexterity, gait and balance.\textsuperscript{75}

Cadmium affects lungs, kidneys, liver and skeletal system. It binds to sulfhydryl groups, displacing other metals from metallo-enzymes, disrupting those enzymes. Cadmium competes with calcium for binding sites on regulatory proteins. Lipid peroxidation has been demonstrated. The IARC has classified cadmium as a human carcinogen (group I) on the basis of sufficient evidence in both humans and experimental animals.\textsuperscript{76} Cadmium has been associated with prostate cancer, but both positive and negative studies have been published. Early data indicated an association between cadmium exposure and kidney cancer.\textsuperscript{77} Furthermore, a population based multicenter study of renal cell carcinoma found an excess risk in occupationally exposed persons.\textsuperscript{78} In summary, the evidence for cadmium as a human carcinogen is rather weak, in particular after oral exposure. Therefore, a classification of cadmium as ‘probably carcinogenic to humans’ (IARC group 2A) would be more appropriate. Adults take up 10–15\% of lead in food, whereas children may absorb up to 50\% via the gastrointestinal tract.

Lead in blood is bound to erythrocytes, and elimination is slow and principally via urine. Lead is accumulated in the skeleton, and is only slowly released from this body compartment. Half-life of lead in blood is about one month and in the skeleton 20–30 years.\textsuperscript{79} In adults, inorganic lead does not penetrate the blood brain barrier, whereas this barrier is less developed in children. The high gastro-intestinal uptake and the permeable blood brain barrier make children especially susceptible to lead exposure and subsequent brain damage. Organic lead compounds penetrate body and cell membranes. Tetra methyl lead and tetraethyl lead penetrate the skin easily. These compounds may also cross the blood brain barrier in adults, and thus adults may suffer from lead
encephalopathy related to acute poisoning by organic lead compounds. The symptoms of acute lead poisoning are headache, irritability, abdominal pain and various symptoms related to the nervous system. Lead encephalopathy is characterized by sleeplessness and restlessness. Children may be affected by behavioral disturbances, learning and concentration difficulties. In severe cases of lead encephalopathy, the affected person may suffer from acute psychosis, confusion and reduced consciousness. People who have been exposed to lead for a long time may suffer from memory deterioration, prolonged reaction time and reduced ability to understand. If the neuropathy is severe the lesion may be permanent. The classical picture includes a dark blue lead sulphide line at the gingival margin. In less serious cases, the most obvious sign of lead poisoning is disturbance of hemoglobin synthesis, and long term lead exposure may lead to anemia. Acute exposure to lead is known to cause proximal renal tubular damage, there is also evidence that certain genetic and environmental factors can increase the detrimental effects of lead on neural development, thereby rendering certain children more vulnerable to lead neurotoxicity.

Physicians and scientists agree that no level of heavy metals in blood is safe or normal. The disturbing fact is that exposure to extremely small amount can have long-term and measurable effects in children while at the same time causing no distinctive symptoms. Another problem of heavy metals exposure is it being cumulative in nature. After they have been absorbed into the blood, some of them are filtered out and excreted, but the rest are distributed in the liver, brain, kidney and bones. The Consumer Product Safety Commission experimentally demonstrated that light and heat can cause degradation of toys and liberation of lead dust but unfortunately for children’s, toys released lead and other metals during normal
product use. Given the known potential toxicity, the serious health effect and the ability of heavy metals, to leach out of children’s toys through contact, the continued use of lead and other heavy metals in children’s toy raises serious concern.

This study determined the physicochemical parameters of leachates of finished plastic products (such as change in the pH of leachates, global migration residue, oxidizable materials, UV absorbing materials and heavy metals). current pattern in the use of lead and other heavy metals as stabilizer in plastic toys and other plastic products using analytical techniques that would yield empirical data. The data collected were used to provide a clear picture of hazardous chemicals in plastic toys and plastic products.
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