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Importance and Applications of Polyethylene Terephthalate wastes in the Coating Industry: A Review

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ABSTRACT: Plastics are found almost everywhere and are indispensable part of the modern era. In such a Polymer centric era, the issues caused by its pollution are inevitable. Polyethylene Terephthalate, PET comprises of the most commonly used polymer with its widespread application in the packaging industry for bottles. With growing environmental awareness, its recycling has become a topic of mainstream research. This paper reviews all the major research carried out in chemical recycling of PET waste across the globe which can be later used in the coating industry. A meticulous study is done so as to describe, compare and discuss the various techniques like methanolysis, glycolysis, and aminolysis etc. which were cured onto air drying systems with isocyanate and also for stoving application by using amine derivatives as curing agent. The future prospective it provides, in reducing our carbon food print and stepping on to closed loop sustainable economy are reviewed thoroughly.

KEYWORDS*:* Depolymerization, Hydrolysis, Glycolysis, Methanolysis, Aminolysis, Recycling, PU, PET

I. INTRODUCTION

Polyethylene Terephthalate is undoubtedly the most widespread polymer used in the world in terms of quantity. It is a clear polyester which is both light, strong with enhanced performance and rigidity with relatively cheap cost. From its evolution in the early 1970s, it has emerged into an indispensable part of modern life. It is a condensation polymer synthesized from terephthalic acid (TPA) or dimethyl terephthalate (DMT) and ethylene glycol (EG) with removal of water molecules and methanol respectively in presence of antimony catalysts [1]. Other than water bottles, few technically demanding applications of Virgin PET includes paper coatings packaging for food and other items, films for touch screens which are abrasion and chemical resistant. It is also used as a substrate in electronic applications such as in spin coating and inkjet printing.

Currently, it also stays at the top of the list of polymers that are recycled. If disposed in landfills, if causes great environment concerns as its non-biodegrade and takes up a lot of space. The major outlet for recovered PET is still the fiber market. Thus, various techniques are used for its reuse, reclamation and recovery of the waste PET bottles. Mechanical recycling involves process like flotation and solution process wherein the mixed polymers and contaminants are separated by their density differences [1].

Fig 1: Scope of PET waste Recycling and Reuse

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Chemical recycling are more common for PET recycling as it degrades the PET chain by chain scission process using water, methanol, glycols, polyamines in hydrolysis, methanolysis, glycolysis and aminolysis respectively using catalysts like zinc acetate and cobalt acetate etc. In addition to it, hydrolysis can be further divided into acidic, neutral or alkaline. All these processes suffer the disadvantages of needing high temperature and pressure for processing. Even then, the post-consumer PET bottles are recycled into carpet, textiles, sheets etc. Scope of using PET wastes for coatings are increasing in demand and we already have companies using these for synthesizing hydroxyl terminated products of depolymerization with acids forming polyester polyols for polyurethane foams [2]. This paper summarizes various works done in PET waste usage in Coating industry in detail. A meticulous study on various research possibilities were thus looked into.

II. CHEMICAL RECYCLING OF PET

Under chemical recycling, even when we have numerous techniques and new ones arising every year, there are four to five notable ones among them.Glycolysis is the treatment of high molecular weight PET with an excess of Glycol in presence of catalysts like zinc acetate at about 180^{0}C to produce hydroxyl-terminated short chain fragments. Here, the ester linkages are broken by the glycols resulting in trans-esterification reaction forming oligomers or oligo ester diols and polyol [1].

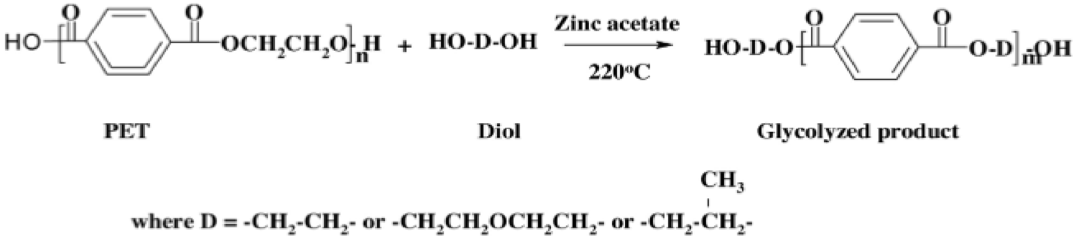

Fig 2: Glycolysis of PET waste (1)

Mainly, it yields bis (2-hydroxyethylene terephthalate) after the depolymerization which later finds it usage in curing with isocyanate or amine systems. In Aminolysis or ammonolysis, polyamines or tri-ethanolamines are respectively used forming bis (2-hydroxyethylene terephthalamide) which also finds similar use in coatings. By using methanol to depolymerize PET waste under high pressure and temperature, it results in the formation of dimethylterephthlate DMT which is in turn a monomer of PET manufacturing [2].

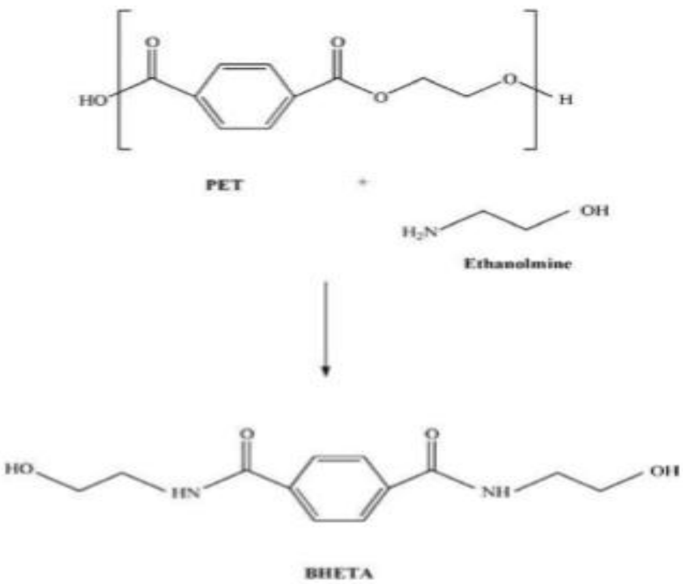

Fig 3: Aminolysis of PET waste (3)

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This process gives in an opportunity for a closed coop recycling of PET but the process is cumbersome with a lot of unit operations combined like filtration, crystallization and distillation with an added danger of using highly explosive methanol in excess. Hydrolysis are of three main types, using water, alkaline solutions and acidic solutions in Neutral, Alkaline and acidic hydrolysis respectively. In all these cases, the monomer Terephthalic acid is effectively recovered whereas ethylene glycol is not. Also, we use strong inorganic acids like nitric acid, sulfuric acid etc. which has to purified using the formation of sodium salt can thus needs highly expensive materials which are corrosion resistant. Same issues demerit the alkaline hydrolysis as well. Also, Solvolysis wherein solvolytic chain cleavage into low molecular products are also explored in detail. In generic words, it can be stated that PET waste can be depolymerized by using any of these methods at high pressures like 20-25 kg/cm3 and temperature ranging from 180-230^{0}C using zinc acetate , manganese acetate etc. [2]. We will look onto to the various literature works carried out in this field which goes into practical application.

III. CURRENT DEVELOPMENTS

Various process of chemical recycling has been instated in the coating industry over the years which has found its benefits and are being applied onto plant scale. Out of these, aminolysis and glycolysis are the most successful ones till date.

Corrosion resistance was a major factor that was improved with the aminolysis process [3]. Using 3-amino- 1 propanol, disposed Pet bottles were reacted in presence of catalyst like sodium acetate to facilitate aminolysis process where in they were depolymerized into bis-(3-hydroxy propyl) terephthalamide (BHPTA) [3]. They were purified in the later stage with e-caprolactone to get long chain saturated polyol. In this process dibutyl-tin-dilaurate (DBTDL) was used as the catalyst. With the polyol derived as the base component and curing with isocyanate to form two pack polyurethane coatings, performance properties observed were remarkable including mechanical and chemical resistance, enhanced hardness and impact resistance. Most striking among them was the anti-corrosive performance as measured by the salt spray test .Characterization of thermal properties using Differential scanning calorimetry (DSC) and Thermogravimetric analysis (TGA) confirmed the findings. Not just amino derivatives, more modifications were seen to have done well during and throughout the aminolysis process such as the formation of polyester amine resins. It includes the usage of jatropha oil which was first treated with dicarboxylic acid like sebacic acid and thus, converted into its corresponding fatty amide, i.e. hydroxyl ethyl jatropha oil fatty acid amide (HEJA) [4]. Later this was treated with the product so obtained by the aminolysis of PET waste, bis(2-hydroxyethyl) terephthalamide (BHETA) and jatropha derivative formed eventually curing it with isocyanates and finds use in coating applications. It had an added advantage of balanced flexibility and hardness. It can be attributed to the structural difference in BHETA and HEJA. BHETA increases hardness and retards degradation because of its aromatic structure. Whereas HEJA increases flexibility due to its aliphatic nature. Adhesion is also seen to be increased greatly by this amine linkage resulting in better mechanical properties and corrosion resistance [4].

Glycolysis is another well-established process in chemical recycling of PET. It has found its use in coating industry both in stoving process for automotive finishes and also in air drying process with isocyanate curing. Automotive coatings are ranked one among the topmost expensive coatings wherein the incorporation of a waste material would be perfect example of a sustainable yet innovative solution. Stoving usually refers to the resin, usually the acrylic or polyester polyols cured by amine derivatives and cooked in oven for specified time. Properties are bound to be immensely heightened in such a process and are now commonly used in automotive coating applications. On carrying out the glycolysis process by using propylene glycol of molecular weight 2000 and later reacting these depolymerized oligo esters into trans-esterification with oils such as castor or jatropha, highly saturated hydroxyl functional polyester polyols were obtained [5]. Melamine formaldehyde resins were used as the hardener component for two pack coating system and stoving was carried out. Cured films, on testing, showed great improvement in hardness and chemical and corrosion resistance. Glycolysis was also confirmed by FTIR characterizations [6].

This list of developing secondary value added resin like alkyds from glycolysis of PET waste us an area that has been scrutinized well by many researchers over the century. It involves using Di-ethylene glycol with different molar ratios. More meticulous work were done by synthesizing unsaturated polyester polyol from then by reacting them further with maleic anhydride, phthalic anhydride and propylene glycol and even mixed with styrene before curing with amine derivate in benzoyl peroxide systems in ambient condition itself, Comparable mechanical properties like tensile and elongation at break were obtained with these cured films [6]. This in turn open up the scope for various modifications that can be done to each sub group under glycolysis.

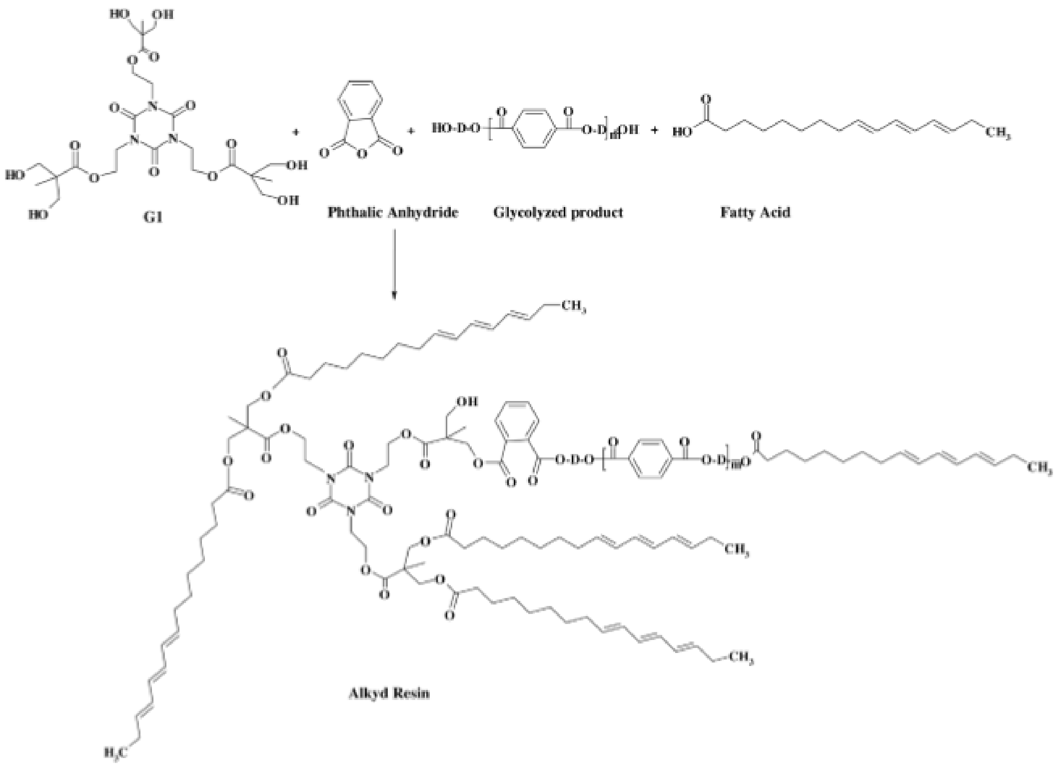

Fig 4: Alkyd resins from PET waste and Bio-derived fatty acids of oils (6)

On increasing PET percentage from 5 % to 10 %, MEK double rub resistance, solvent and chemical resistance and corrosion resistance all were seen to increase. Also, lower corrosion current densities were clearly shown by the potentiodyamic polarization study, i.e. reduced corrosion rate, there confirming dense coating formation with castor oil and PET waste based system [6].

More generic form of glycolysis involved the isocyanate curing systems. Further starch derived glycol glycosides were used for depolymerization and later the oligomers so formed were further reacted with Soya oil fatty acid SOFA to obtain urethane coatings. These were used in industrial maintenance finishes and found to be giving tremendous improvement in properties [7]. More versatile alkyds were also formed with the same process of glycolysis of PET waste and bio resources such as linseed oil and sunflower oil fatty acids. From the so cured films, it had enhanced properties in terms of adhesion, bending, impact and ductility coupled with good gloss and hardness which were seen to be dependent on the degree of branching and the molecular weight of resin in the backbone of the polymer. Usage of these polyol based on PET waste, i.e., BHET, better thermal stability and film properties were obtained. Initial decomposition temperature of all these cured films mentioned above were seen to be more than 200 ^{0}C with the help of TGA curve, thereby showing its wide acceptance in coating industry. Few researchers also evaluated the changes in properties on using potassium acetate (1% w/w of the total raw materials) as catalyst and the ratios chosen to understand trend in yield increment [8].

IV. CONCLUSION

By recycling PET waste, we are not only giving a partial solution to the solid waste problem but also giving a vast scope for a new raw material to many industries including paint and coating Industry. Even now, fiber industry still remains as the highest consumer of PET waste to be used polyester textiles. PET recycling reduces our dependence on petroleum derived p products and energy. As it’s a replenishable resource, any step towards reducing our dependence on such resources are worth looking into by dedicating our time, energy and money. We saw above the various techniques used around the world by scientist to come out with value added product from PET waste. It has a huge scope of further

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research and of implementation in companies. The processing constraints like the high temperature, high pressure and explosive chemical usage needs to be accommodated by proper process control measures, advanced reactor designing and taking up all necessary precautions. With the rate of advancements going on in the plastic industry right now, it's just a matter of time when at least one such process is carried out in huge scale effectively. Amongst the varied options, BHET from Glycolysis seems to be better for air drying isocyanate curing systems and aminolysis could be preferred for stoving applications with amine derivatives.

Many improvements are being ferociously carried out in the sustainability of materials used in the coatings industry. This can be attributed to the growing environmental, safety and health concerns which is gaining interests as people get more awareness about it by various programs put forward by governments of different countries. The concept of a circular economy by stewarding better global resources throughout are just the part of a larger movement towards recycling. More concentration is given by the researchers on a non-petroleum dependent, bio-resources like natural oils etc. to add properties to the recycled PET and to come up with economical yet efficient high performance Industrial coatings. Reclamation, Recycling and reuse of materials are undoubtedly the key to the progress of any country into a profitable and sustainable economy.

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Jomin Thomas, M.Tech Polymer Technology from CUSAT,Kerala and Chemical Engineering from Visvesvaraya National Institute of Technology, India. Received summer industrial training from Astra Polymers Compounding limited in B.Tech and in Asian Paints Research and Technology Centre, Mumbai. Got highly interested in polymers, coatings and materials science field even more from then and looking for more opportunities for gaining more knowledge. Closed loop polymer recycling is my dream and my passion both.