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Degradation of fundamental polymers/plastics used in daily life: a review

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ABSTRACT
Polymers/plastics, composed of monomers in the form of chain/s, are one of the highly used materials for different purposes in daily life. Abiotic and biotic processes carry out degradation of polymers. Abiotic pathway occurs from thermal, catalytic and photo-degradation methods whereas biotic methods occur in presence of different type of microorganisms. The degradation of representative polymers; petro- and bio-based (polyethylene and polylactic acid respectively) was explained by thermal, catalytic, biodegradation and photo-degradation processes. The thermal degradation of polyethylene and polylactic acid was explained by thermogravimetric analysis (TGA) curves. Catalysts such as zeolites and amorphous silica-alumina were used for degradation of polyethylene whereas, tin for polylactic acids. Microorganisms such as bacteria, fungus and *actinomycetes* help for degradation of polyethylene and polylactic acid. Ultra violet (UV) radiation and hydroperoxides are used for the photo-degradation of polymers. Bio-based polymers are found to degrade relatively faster into environmentally compatible fragments in comparison to petro-based polymers. Therefore, it is emphasized on producing bio-based polymers rather than petro-based for sustainability for addressing plastics related global environmental issues.

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1. Introduction

Daily human life without polymers is hardly expected these days because polymers have become one of the essential materials of twenty first century. Natural (bio-based) and synthetic (petro-based) polymers are being widely used in these days in daily life. The worldwide estimated quantity of plastics production is increasing from 325 million tons (today) to 1100 million tons by

2050. Most of the plastic materials will end in landfills and more is incinerated till today even though the rate of recycling is going up day by day. Numbers of researches are being carried out for the disposal and degradation of polymers and plastics. Re-use, and recycling of plastics followed by the production of bio-based eco-friendly plastics can be the sustainable tasks for upcoming human generation [1,2]. In these days, natural polymers such as cellulose, chitin, lignin, starch, pectin, natural fibers etc. and the secondary materials based on them are the research topics of scientists for different applications such as drug delivery, biocompatible dental, and surgical implants etc. [2]. Similarly, many synthetic plastics such as polyethylene (PE), polyvinyl chloride (PVC), polystyrene (PS), polypropylene (PP) etc. are being used for packaging and other household applications because of their low weight, low cost and durability [3,4]. Meanwhile, they contribute to the existing disposal and degradation problems in maximum. Their manufacturing includes different organic and inorganic materials such as carbon, hydrogen, oxygen, nitrogen, chlorides, coal and natural gases [3-5].

Polylactic acid (PLA), one of the most widely used bio-plastic, exhibits high stiffness, low toughness, transparency, biocompatibility, biodegradability etc. [5]. It has a very slow crystallization rate containing high level of crystallinity as end products that dictates most of the mechanical and thermal properties [6,7]. The ductility and toughness of PLA have been improved following multiple strategies such as copolymerization, plasticization, melt blending etc. with different tough polymers, rubbers and elastomers [6-11]. PLA is available in the market at a price on a par with that of common plastics like polypropylene [5].

Polymer degradation can be a set of complicated processes whose actual mechanism/s has not been explained till now. Mostly, the degradation of polymers occurs by abiotic or biotic pathways. Abiotic pathways refer to thermal, photochemical and oxidative processes whereas microorganisms and enzymes carry out biotic degradation [12-14]. Photodegradation of polymers also occurs *via* homolytic bond celevage of ester like bonds followed by free radical chain mechanism in presence intense solar UV radiations [12,14].

Biodegradation (enzymatic degradation) of polymers by the action of metabolic microorganisms such as bacteria, algae and fungi etc in presence of atmospheric oxygen from which small molecules or fragments are released into environment. This process is based on the concept of 'Carbon Neutrality' by which the generated carbon dioxide is again converted into biomass by photosynthesis [15-21]. Chemical structure, functional groups, reactivity, swelling behavior hydrophilicity etc are the factors affecting the biodegradability of polymers [22,23]. *Pseudomonas*, *Streptomyces*, *thermoactinomycetes*, *Klebsiella*, *Actinomycetes*, *Nocardia*, *Micromonospora*, *Flavobacterium*, *Comamonas*, *Escherichia*, *Mycobacterium*, *Rhodococcus*, *Azotobacter*, *Alcaligenes*, etc., are the common bacteria identified contributing to polymeric biodegradation [23,24]. Similarly, *Sporotrichum, Talaromyces, Thermoascus, Thielavia, paecilomyces, Phanerochaete, Ganoderma, Geotrichum, Cladosporium, Phlebia, Trametes, Candida, Penicillium, Chaetomium, Aerobasidium*, etc. are the fungi identified so far taking part in polymer degradation [25,26]. It has been found from the research works that bio-based polymers degrade earlier in comparison to petro-based polymers/plastics [23].

This paper presents a brief review on advances in degradation of PLA and PE as representative examples of bio-based and petro-based polymers respectively. Thermal, bio- and photo-degradation of these polymers along with some results/data from the literature are taken into account for the discussion. The idea will be supportive to focus the polymeric research particularly on bio-based polymers, finding the cross-linking reagent/catalyst

that easily polymerizes the corresponding bio-monomers to bio-polymers for future prototype materials building, and the sustainability. It will also be useful to explain the real mechanism of polymer degradation and composting phenomenon that is remained poorly defined in polymer research till yet.

2. Thermal degradation of PE

Thermal degradation of polymers is experimentally performed under an inert atmosphere and the process is called pyrolysis/thermolysis. The most commonly followed method is the thermogravimetric analysis (TGA). In this method, 15 to 20 mg of polymer, taken in a platinum pan hanged with a spring is heated up to 600℃ [27-29]. Abbas-Abadi (2020), reported the degradation of PE at 650-850 K in N_2 atmosphere at the heating rate of 30 K min^{-1} [30]. The TGA curve of PE is presented in Fig. 1 [28].

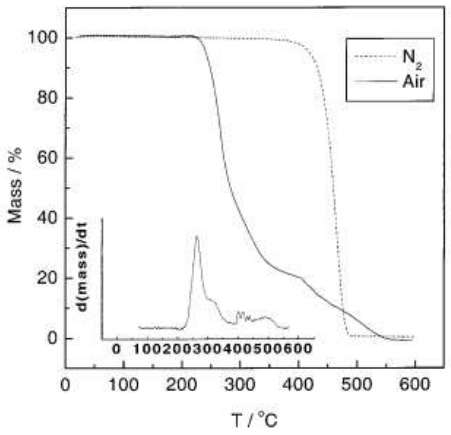

Fig. 1: TGA curves of PE under nitrogen (dashed line) and air (solid line) (heating rates of 9.2 and 9.0 K N min^{-1} for nitrogen and air, respectively). Inset: derivative plot of weight loss for degradation in air [28].

Figure 1 shows that PE is degraded in a single step that begins at 350℃ and reached zero mass at 490℃ in N_2 atmosphere. However, degradation curve possesses some irregular trends in presence of air. The degradation of PE begins at 220℃ and reaches zero mass at 550℃ that might be for the oxidation at first, and degradation steps at the end.

The thermal degradation of PE in presence of catalysts performs different behavior with respect to product yield. The catalysts such as zeolites, amorphous silica-alumina etc. are used for effective thermal degradation of PE for the increased rate of reaction [31-34]. The use of amorphous silica-alumina, during thermal degradation of PE significantly reduced the activation energy in comparison to thermal processes without catalyst/s [33-40]. The catalyst (10% by w/w of polymer catalyst ratio), dependent yields of thermal degradation of PE at 560℃ are presented in Table 1.

3. Thermal degradation of PLA

The mechanism of PLA degradation by pyrolysis is shown in Fig. 2. The thermal degradation of PLA is a complex phenomenon consisting of a random main-chain scission and unzipping or decompress depolymerization reaction [41-44]. The random degradation involves intramolecular and intermolecular trans-esterifications, cis-elimination and other reactions such as hydrolysis or oxidative degradation whereas, unzipping or decompress depolymerization occurs when terminal hydroxyl groups became more concentrated [42,44-46].

Thermal degradation of PLA is also studied using thermogravimetric analysis (TGA) [47-51]. The heating rates of 5, 10, 20, 30, 40℃ min^{-1} were used which is shown in Fig. 3 (a). The TGA curves of PLA showed single decomposition peak at lower heating rate, the retention time required for the PLA to a given temperature is longer [52]. The pyrolysis of PLA was carried out in presence of catalyst. Many researchers have explained the effect of catalyst in pyrolysis behavior of PLA in literatures [44,52-57]. Organo-catalyst such as 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD) and 4-pyrrolidinopyridine also helps in degradation of PLA [58]. The TGA curves for pyrolysis of PLA in presence of tin as catalyst is shown in Fig. 3 (b) which shows that the degradation temperature for PLA decreases as the composition of tin increases [53].

Table 1: Catalyst dependent product yield in the pyrolysis of PE at 560℃ [40].

Catalyst	Percent Products				
	Ethylene	**Propylene**	**Isobutylene**	**1-hexene**	**Heptane**
None	39.98	19.52	19.41	17.24	12.84
Al_2O_3 (basic)	29.02	15.53	18.20	22.57	15.61
Al_2O_3(neutral)	25.67	15.21	17.59	24.09	17.43
SiO_2	26.39	11.48	17.70	22.97	13.40
Zeolite	23.19	11.39	17.39	28.40	17.04

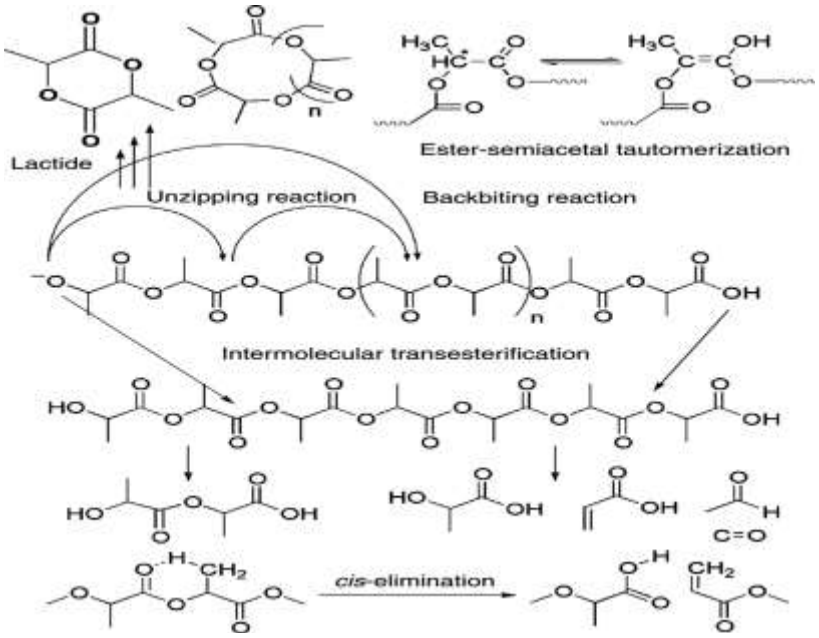

Fig. 2: Thermal degradation of PLA and pyrolysis mechanism [44].

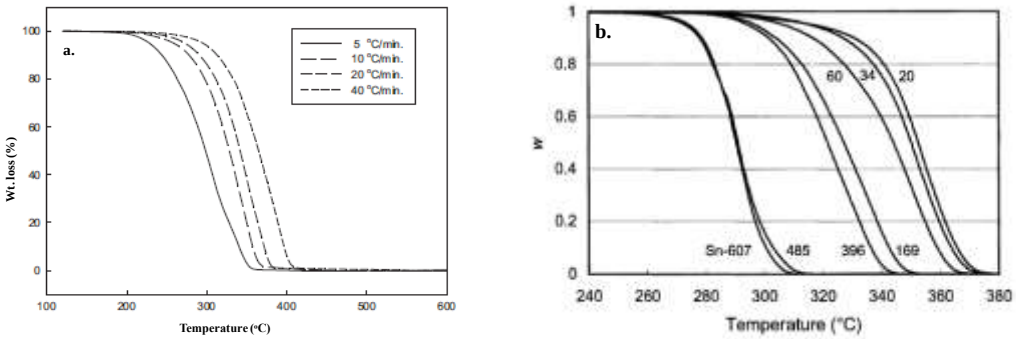

Fig. 3: (a) TGA curves of PLA at different heating rates (5, 10, 20 and 40℃ min^{-1}) under N_2 (b) TGA curves of PLA-Sn samples at a heating rate of 5 K min^{-1} under N_2 flow of 100 mL min^{-1} [52,53].

Thermal degradation of bio-based polymer and petro-based polymer occurs by pyrolysis in presence of air or nitrogen. Various catalysts support the pyrolysis mechanism. Catalyst such as zeolites and amorphous silica-alumina are used for degradation of polyethylene whereas, tin for polylactic acid. The temperature required for pyrolysis of polyethylene in presence of catalysts is higher than that of polylactic acid. Therefore, degradation of bio-based polymers required less energy and faster process than petro-based polymers.

4. Biodegradation of PE

PE is a representative of synthetic homo-polymers that contain repeating units of $-CH_2-CH_2-$ as a monomer in the polymer backbone [3]. Biodegradation/composting of homopolymers is reported to occur in decades by bond cleavage with the enzymatic action of microorganisms [59]. The degradation of $-CH_2-CH_2-$ backbone can be enhanced by the addition of readily biodegradable compounds, such as starch, to a low-density polyethylene matrix etc. [15].

Some researchers have explained the composting and biodegradation as synonymous terms but others have different arguments that in composting not only the solo microorganisms but also the microorganisms, enzymes, fungi, heat, temperature, light and moisture acts simultaneously for the degradation [60-65]. Devi *et al.* (2015), Hadad *et al.* (2005), Abrusci *et al.* (2011), Sowmya *et al.* (2014), Nowak *et al.* (2011), Usha *et al.* (2011), Bonhomme *et al.* (2003) and Sepulveda *et al.*(2002) studied the role of different temperature dependent microorganisms and corresponding enzymes for PE degradation. It has been reported that PE breaks down into simpler products (after decades) such as in biofilms, esters, unsaturated hydrocarbons, alkylhalides and others as listed in Table 2 [59-66]. The comparative study of mechanism of bio-degradation and surface morphology of polymers was also explained by spectroscopic, microscopic and thermogravimetric methods.

Similarly, fungal degradation of PE is explained by Corti *et al.* (2010), on the basis of Fourier transform infrared spectroscopy (FTIR) which is presented in Fig. 4 [67].

The FTIR peaks of polyethylene before and after degradation is different. The dotted line expressed the degradation of polyethylene in 6 month. The FTIR spectra from polyethylene films by the fungal degradation enhance the formation of small units containing carbonyl groups. The FTIR breakdown products in pre-oxidized polyethylene films as reflected by peak intensities on several functional groups. In FTIR spectra several peaks shows the various functional groups such as –C=O (1743 cm^{-1}), -C=C- (1640 cm^{-1}), -OH deformation vibration (1080 cm^{-1}) and -OH stretching vibration (3400 cm^{-1}). The appearance of new bands were possibly due to the oxidized fractions such as moieties containing -OH groups, resulting from the fungal biodegradation [67].

5. Biodegradation of PLA

PLA is a bio-based polyester derived from starch feed stocks with a hydrolysable backbone that is susceptible to biodegradation. It is the promising candidate of biodegradable plastic [68] whose biodegradability is based on bacteria such as *Bacillus stearothermophilu*, *Geobacillus thermocatenulatu*, fungus, *actinomycetes* etc. and biochemical processes of degradation have been advanced in recent years [69]. PLA undergoes biodegradation both in aerobic and anaerobic conditions [69]. It is a complex chemical hydrolysis process in presence of soil microorganism in which ester bonds of PLA cleavage into carboxylic acid and alcohol with hydrion (enzyme) [69]. The different steps and possible mechanism of degradation is summarized in Fig. 5.

As in Fig. 5 during biodegradation, PLA-degrading microorganisms first produce extracellular depolymerase of PLA that requires some inducers like elastin, gelatin, silk fibron and some peptides and amino acids [69-71].

Table 2: List of some microorganisms and corresponding enzymes contributing to PE degradation.

Microorganisms	PE degrading enzyme	Evolution of new compounds	Temperature (℃)	References
Aspergillus tubingensis	-	Biofilm	45	[60]
Brevibacillus borstelensis	-	Biofilm	30, 45 and 50	[59,61]
Trichoderma harzianum	Laccase, manganese peroxidase	Carboxylic acids, aldehydes, esters, ethers, and alkyl halides	50	[62]
Gliocladium viride, *Aspergillus awamori* and *Mortierella subtilissima*	Bionolle	Unsaturated hydrocarbon and saturated hydrocarbon	27	[63]
Streptomyces sp, *Psudomonas sp*, *Bacillus*, *Staphylococcus sp* and *Aspergillus sp*	-	-	30	[64]
Rhodococcus rhodochrous	-	Biofilm	60	[65]
Aspergillus niger and *Penicillium pinophilum*	Extracellular enzyme	-	80	[66]

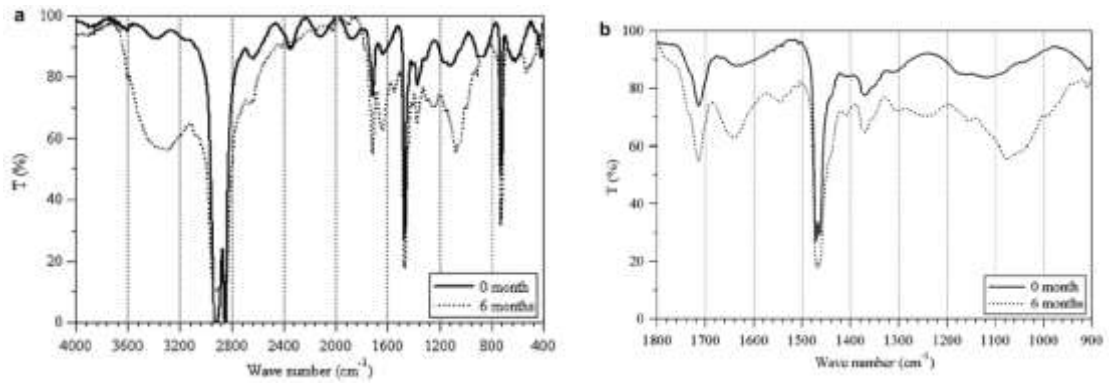

Fig. 4: (a) FTIR spectra of control and pre-oxidized PE films incubation with fungal strain for 6 months (b) magnified region of the spectrum between 900 and 1800 cm^{-1} of Fig. (a) [67].

The inducers contain L-alanine units, which is similar to L-lactic acid units of PLA. Depolymerase enzyme attack ester units of PLA resulting in the formation of oligomers, dimers and monomers. Finally, it decomposes to carbon dioxide, water and methane [71-74]. Some PLA degrading microorganisms and their corresponding degrading enzymes have been shown in Table 3. Results show that protease is the major enzyme that most of bacteria produce for PLA degradation at 30 ºC [75-80].

Chaisu *et al.* (2013) studied the surface morphology of PLA film after 30 days at 30℃ by the growth of *Aneurinibacillus aneurinilyticus* on samples. The surface morphology of PLA film was observed by SEM analysis in secondary electron mode as in Fig. 6 and shows that the PLA film surfaces were smooth in controls before inoculation. However, after bacterial incubation within 30 days shows the surfaces as rough and hemispherical holes as in Fig. 6(b). These SEM micrographs support the PLA films degradation by *Aneurinibacillus aneurinilyticus* at optimal

laboratory conditions. Pranamuda *et al.* (1997), also observed the similar surface morphology of PLA by *Amycolatopsis sp* [81,83].

The degradation time of bio-based polymers and petro-based polymers is different. For complete degradation, petro-based polymers take a several years and decades as compared to bio-based polymer degradation [84-90]. A comparative study of polymer thin film degradation time in soil has been presented in Table 4. For a complete degradation of polymers in soil takes several years and also depends on thickness of plastic, type of microbes, temperature, moisture content, pH of soil and soil humus. A thin film of polylactic acid in soil was degraded in 30-35 days and that of polyethylene film in 60-65 days [84,88]. Further, the ether or ester bond containing polymers were degraded earlier as compared to the other hydrocarbon homo polymers.

Above results revealed that both bio-based and petro-based polymers under goes degradation by various microorganisms under different conditions. Microorganisms such as *Psudomonas sp and Bacillus* helps for maximum degradation of polyethylene as compared to other microorganisms [64]. Similarly, *Brevibacillus sp* for degradation of polylactic acid [78]. The time required for degradation of bio-based polymer film is less as compared to petro-based polymers. Further, polymers containing the ester, peptide or ether linkage degraded easily in soil with biocompatible end products as compared to hydrocarbon homopolymers. The exact degradation mechanism, isolation and culture of polymers specific bacteria and optimization of conditions for degradation and composting has not been fully studied and practiced till yet, and created the problems for the sustainable polymer waste management.

6. Photo-degradation of PE

It is reported that photo-degradation of most of polymers occurs in presence of highly energetic UV radiation following the mechanism of free radical formation similar to that of peroxidation reaction [91-94]. UV radiation with wavelength range of 290-400 nm can degrade PE into small units compatible to soil such as esters and lactones in presence of hydroperoxide [92,95] as presented in Fig. 7.

7. Photo-degradation of PLA

Photo-degradation of Polylactic acid is also carried out in presence of strong UV radiation (200-400 nm) with the formation of anhydride and carbonyl groups at the end as final product [96-100]. Bocchini *et al.* (2010) explained the mechanism of photooxidative degradation of PLA by the chain excision (intrachain β-scission). The photo-degradation of PLA also occurs by Norrish I and II type cleavage, followed by the formation of carbonyl groups as explained in Fig. 8 [97,98]. In this mechanism the anhydride groups are formed by radicals that react with oxygen and extract a hydrogen forming hydroperoxide [98-100].

The photo-degradation of petro- and bio-based polymers more often than not takes place in presence of UV radiations. The polyethylene is not easily decomposed to esters and lactones since it requires large amount of energy and high mechanical pressure. The photo-degradation of polylactic acid is relatively easier with esters and acids as common end products. Therefore, bio-based polymers as well as the polymers containing the ester, peptide, ether, carbonyl or amide linked polymers are relatively easier for photo-degrdadation to soil compatible products as compared to polyethylene, polyvinyl choloride, polypropylene polymers.

Recommendation for future work

Many researchers proposed and explained polymer degradation in different ways. However, none of them is found absolute with respect to time, cost as well as environmental concerns. Although composting or biodegradation of polymers seems to be an effective solution of polymer waste disposal, the exact degradation mechanism, isolation and culture of polymer specific microorganisms in laboratory is still missing. This review recommends researchers/readers to focus on green techniques/catalysts for polymerization of natural and bio-based monomers that contain the carbonyl, peptide or ether linkage, and easily degrades by composting or low intensity of UV radiations forming the eco-friendly end products.

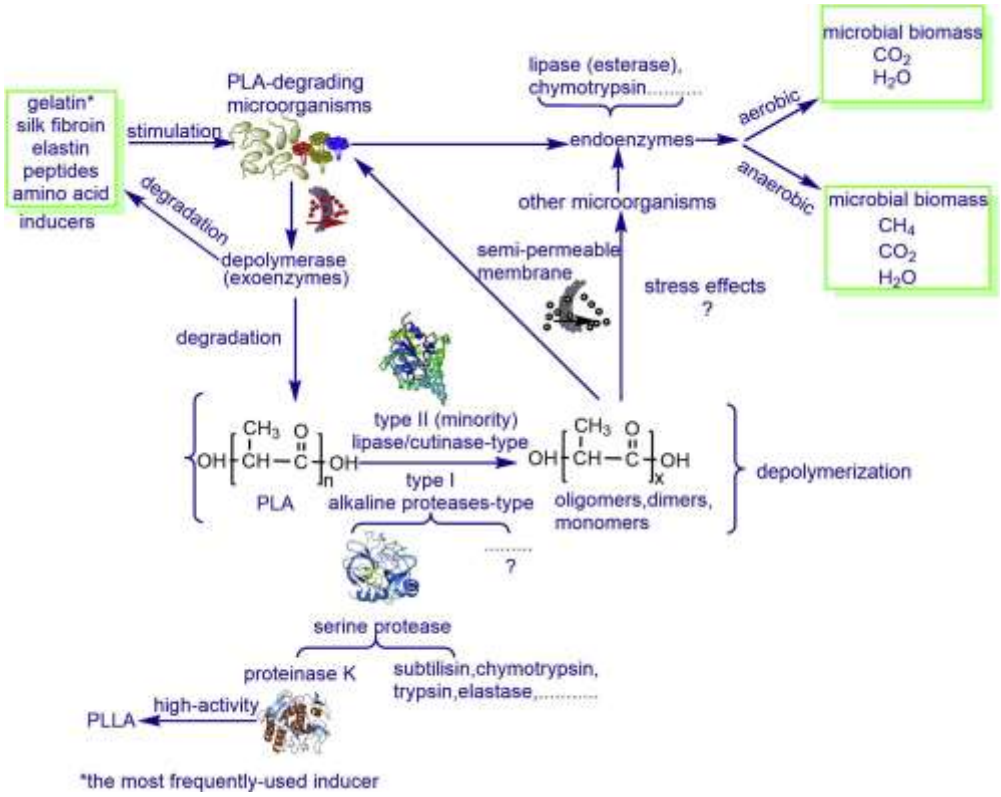

Fig. 5: Schematic diagram of biochemical processes in PLA degradation [Qi *et al*. (2017)].

Table 3: PLA degrading microorganisms and corresponding enzymes.

Microorganisms	PLA degrading enzyme	Evaluation of degradability	Optimum Temp. (℃)	References
Amycolatopsis sp. strain 3118	Protease	L-PLA, film weight	30	[75]
Amycolatopsis sp. strain 41	Protease	L-PLA, silk powder, casein, film weight	30	[76]
Lentzea waywayandensis	Protease	L-PLA, film weight	30	[77]
Kibdelosporangium aridum	Protease	L-PLA, film weight	30	[78]
Bacillus stearothermophilus	-	D-PLA, film (TOC, GPC, viscosity)	60	[79]
Brevibacillus sp.	-	L-PLA, film (TOC, GPC, viscosity)	60	[78]
Aspergillus oryzae RIB40	Cutinase	DL-PLA, turbidity of emulsion	37	[80]
Aneurinibacillus Aneurinilyticus	-	PLA film	30	[81]
Geobacillus thermocatenulatus	Protease	L-PLA	60	[82]

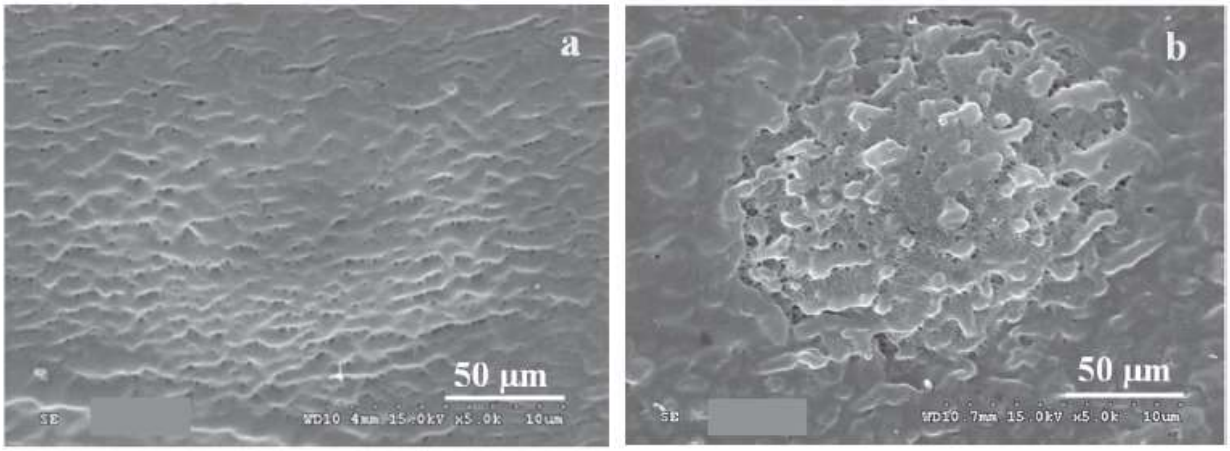

Fig. 6: SEM micrographs showing the surface morphology of PLA films after degradation by bacteria in 30 days at 30 ˚C in liquid medium: (a) surface structure without cell inoculations, 50 μm (control no microorganism degradation), (b) surface structures with cell inoculation.

Table 4: Degradation time of some polymer films in soil.

Polymer film	Degradation span (days)	References
Polylactic acid	30-35	[84]
Polycaprolactone	35-40	[85]
Chitin	160-168	[86]
Cellulose	28-30	[87]
Polyethylene	60-65	[88]
Polyvinyl chloride	90- 95	[89]
Polystyrene	70-85	[90]

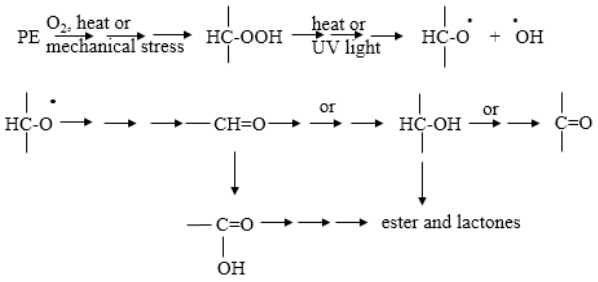

Fig. 7: Peroxidation mechanism of photodegradation of PE [92].

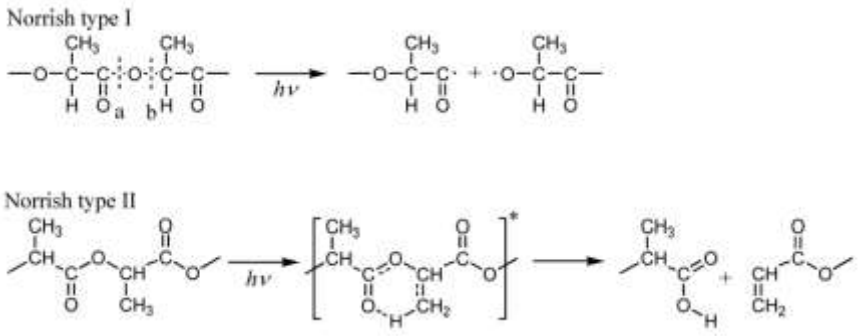

Fig. 8: Degradation of PLA by Norrish I and II type reaction [98].

8. Conclusion

In this review article, most common methods for polymer degradation that are familiar in practice such as thermal, photochemical, biochemical and enzymatic/catalytic processes have been discussed in brief taking polyethylene (PE) as a representative example of petro-based thermoplastics polymer and polylactic acid (PLA) as bio-based polymer. Comparing the results related to time, feasibility, cost and environmental concerns the biodegradation with composting would be the better solution of reducing plastic pollution for the sustainability. Results related to composting or biodegradation showed that the bio-based polymers such as PLA, polyhydroxybutyrate, copolyesters degrades easily in to environmentally compatible fragments/monomers as end products in comparison to petro-based polymers although there is very large gap in their mechanical properties. The identification of catalysts and enzymes to polymerize or crosslink the bio-based monomers to replace petro-based commodity polymers and finding the specific polymer eating (degrading) microorganisms would be the best way for the sustainability of polymer research.

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