



# Understanding the controlled biodegradation of polymers using nanoclays



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## ABSTRACT

The main objective of this work is to develop an innovative way to control the biodegradation of polymers using naturally occurring nanoclay to create an eco-friendly method to obliterate polymers instead of incineration. Poly( $\epsilon$ -caprolactone) (PCL), poly(lactic acid) (PLA) and polyurethane (PU) have been taken as representative polymers having ester and urethane linkages whose rates of biodegradation are regulated (both increase and decrease) using organically modified nanometer dimension clays in enzyme media. The extent of biodegradation was measured as a function of time using spectroscopic method as well as weight loss measurements. Photographic image and electron microscopy have been employed to verify the controlled biodegradation in enzyme media. Calorimetric and diffraction studies support the synchronized biodegradation as observed through kinetics and morphology. The mechanism of controlled biodegradation has been established by evaluating the depolymerase activity of polymers in different pH environment which in turn was generated in solid phase by incorporating the nanoclays in polymer matrices. Therefore, nanoclays control the biodegradation of different polymers in a definitive time frame. Serine mediated hydrolysis/cleavage by the enzyme has been highlighted and alteration of enzyme configuration under varying pH induced by nanoclays has been projected. Moreover, a model has been proposed for the controlled biodegradation of polymer induced by different nanoclays.

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## 1. Introduction

Environmental concern over plastic wastes has become a serious issue in last two decades. Petroleum derived plastics are manufactured specifically for their mechanical, thermal stability and durability. Their uses are greatly acknowledged as long-lasting polymers but they do not degrade at all owing to their chemical framework. On the other hand, ephemeral applications such as packaging, catering, surgery, hygiene uses in medical need to be back to environment especially because of their large volume used in societal need. Poly(vinyl chloride) waste of 435, 435 and 1686 kilotons annually are disposed in USA, Japan and China, respectively [1]. After use, these plastics are fed into the environment as waste without attaining its half-life via the process of littering, dumping, landfills, wildlife ingestion and incineration. Oceans are recognized as a major sink for deposition of polymeric wastes [2] and macroplastics are ended up as microscopic granular or fiber-like fragments known as microplastic, progressively

accumulating in the ocean bed [3]. Uptake of microplastic by marine organisms leads to bio-magnification through food web and causes death of fishes, marine birds and reptiles in addition to the extinction of endangered species. Landfill disposal of plastics emits 253 g CO<sub>2</sub> per kg while incineration releases 673–4605 g kg<sup>-1</sup> of CO<sub>2</sub> [4]. However, the process of incineration is the worst option in terms of global warming through huge emission of greenhouse gases. Incomplete combustion of plastic generates carbon monoxide and another harmful gas, while ingestion of plastic spoils wildlife. Small size microplastics with relatively large surface area destroy the fertility of soil and inhibit the growth of flora, fauna and indigenous microbes. Therefore, plastic disposal has become a major issue with its increasing demand in modern life. This is need of the hour to explore biodegradable polymer to replace the petroleum based conventional plastics and has received considerable attraction in recent years.

Development of novel biodegradable polymeric system needs the combination of stiffer and tougher by design along with the controlled or regulated degradation rate. Nanohybrids especially using two-dimensional nanoclay might be emerging materials either in terms of thermal and mechanical stabilization or

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biodegradation of polymer. Biodegradation is considered to be a biochemical process carried out by integrated approach of micro-organisms and/or their biochemical catalytic products such as enzymes. The types of enzymes involved in hydrolysis of ester bonds are esterase [5], proteinase K [6], lipase [5,7], cutinase [8,9] ureases and proteases [10]. In addition, a spectrum of polyester degrading microbes have also been characterized as fungi and different bacteria [11–13]. These biological agents have the strong ability to disintegrate selective organic matters into the end products of CO<sub>2</sub> and H<sub>2</sub>O [14]. Being hydrophobic in nature, most bioplastics cannot pass through phospholipid cell membrane of microbes due to bulky nature of the polymers. Therefore, these long and bulky polymers are first degraded to oligomers and subsequently to simpler and soluble monomers by extracellular enzymes produced by the micro-organism. The low molecular weight soluble monomer easily diffuses through cell membrane and consumed as source of carbon nutrient to generate free energy which further utilized for their growth and metabolic process [15]. Thus, cellular metabolisms transform complex organic bioplastics into simpler inorganic end product and biomass. Entire metabolic processes are governed by enzymes which are secreted by the microorganism. Therefore, nature and action of enzyme produced by the microorganisms are highly selective and specific process depends on the type of bond present in the substrate and physico-chemical conditions of the media [16]. It is essential to understand the degradation mechanism using realistic environmental conditions before implementing a particular biodegradable polymer for specific application. The idea of using nanoparticle to regulate the environment or media to dictate the action of enzyme might be effective and need to be explored in detail.

Organically modified nanoclays having characteristics of large surface area and suitable chemical modification can well be dispersed in polymer matrix. It acts as nucleating agent and control the spherulite dimension of polymer matrix in addition to better interfacial adhesion in nanohybrid [17,18]. Poly(lactide (PLA)-montmorillonite micro- and nanohybrids were synthesized based on the quality of dispersion using unmodified and organically modified nanoclays, respectively, through melt mixing [19,20]. Pure polymer and composites were subjected to accelerated hydrolytic degradation at pH 10.5 over a temperature range of 50–70 °C and found higher rate of degradation for amorphous PLA and its composites [21]. One of the efficient ester specific enzymes is lipase which catalyzes long chain containing carbon ester bonds, constitute a ubiquitous group of enzyme categorized under the class of hydrolase family [E. C. 3.1.1.3]. Although, lipase catalyzed reactions are not only formed acyl enzyme intermediate but also react with thioesters or activated amines, which expands the synthetic potential of lipases considerably [22]. Further, the enzymatic biodegradation rate of PCL had enhanced dramatically in presence of nanoclay under controlled conditions [23]. Shinozaki et al. [9] cloned the PaE enzyme coding gene in *Saccharomyces cerevisiae* isolated from *Pseudozyma antarctica* JCM 10317 which exhibits a strong degradation activity for biodegradable plastics such as poly(butylene succinate), poly(butylene succinate-co-adipate), poly( $\epsilon$ -caprolactone) and poly(lactic acid). Liang et al. [24] had reported *in vitro* enzymatic degradation rate of poly(glycerol sebacate) based materials approximately 0.6–0.9 mm/month in the tissue culture medium which was higher compared to the buffered solution at the optimum pH 8. Kinetic analyses by <sup>1</sup>H NMR spectroscopy of poly(L-lactic acid) with proteinase K enzyme showed 20% release of lactic acid whereas 70% of the core degraded within 48 h for block copolymer micelles of poly(N-(acryloyloxy)succinimide-co-N-acryloylmorpholine)-b-poly(L-lactic acid) [25].

In the present work, biodegradable nanohybrids of poly(lactic acid) (PLA), poly( $\epsilon$ -caprolactone) (PCL) and polyurethane (PU) with

several organically modified nanoclays have been synthesized via solution route to regulate their rate of biodegradation using various nanoparticles in enzyme media. The evidence of controlled and regulated biodegradation has been shown through morphological, thermal and diffraction studies. The mechanism of biodegradation in presence of nanoclays has been worked out in details.

## 2. Experimental

### 2.1. Materials

Poly( $\epsilon$ -caprolactone) (PCL;  $M_w = 65,000$ ;  $PDI = 1.52$ ) from Sigma–Aldrich was used as received for this work. Poly(lactide (PLA;  $M_w = 1.7 \times 10^5$ ,  $PDI = 1.76$ ) from Dow–Cargill was used as received for this work. Polyurethane (PU) was synthesized using poly(tetra methylene glycol) (PTMG) (Terathane, Sigma Aldrich; number average molecular weight ( $M_n$ ) 2900 g/mol), 1,6-hexamethylene diisocyanate (HMDI; Sigma Aldrich) and 1,4-butanediol (BD) (Merck, Germany) as the chain extender at 70 °C for 24 h in an inert atmosphere. The details of the preparation have been mentioned elsewhere [26]. The catalyst dibutyltindilaurate and solvent dimethyl formamide (DMF) were purchased from Himedia and Loba Chemie, respectively. The enzyme, *Pseudomonas cepacia* Lipase was obtained from Sigma–Aldrich, USA. Three different types of organically modified nanoclays were used based on montmorillonite (Southern clay, U.S.A, CEC 110 meq./100 g), ion-exchanged with methyl tallow bis-hydroxyethyl quaternary ammonium (30B), dimethyl dihydrogenated tallow quaternary ammonium (15A) and dimethyl-octadecylamine (C18). The chemical structures of the organic modifiers and nature of nanoclay have been shown in Scheme 1.

### 2.2. Nanohybrid preparation

The nanohybrids of PLA and PCL were prepared via solution route by dissolving polymer in dichloromethane (DCM) solvent and PU was dissolved in dimethyl formamide (DMF). In all the cases, 4 wt.% (with respect to polymer weight) of nanoclays were used to prepare the nanohybrids after dispersing them in polymer solution. The solution was sonicated for 30 min to ensure good dispersion and proper mixing of nanoclay with polymers. Films of nanohybrids were prepared after evaporating the solvent at 60 °C. The films were melted followed by quenching in ice water, to maximize the amorphous content, followed by dried under reduced pressure. Henceforth, we will term the pure organically modified clays as 15A, 30B and C18 and their corresponding nanohybrids as PCL-15A, PCL-30B and PCL-C18, respectively, and so on for the other two polymers (PLA and PU). In all cases, 4 wt.% of nanoclays were used to prepare the nanohybrids.

### 2.3. Depolymerase activity

Fifty milligrams of respective polymers were dissolved in 3 ml of dioxane at 45 °C to make clear solution and was added drop by drop in water at room temperature and was sonicated simultaneously using sonic oscillator for 30 min. Ultimate concentration of polymer suspension was kept at 0.5 mg/ml for optimum dispersion. Polymer suspension was used for the studies of depolymerase activity. Depolymerase activity was measured spectrophotometrically at different pH 5, 5.5, 6, 6.5, 7, 7.5, 8, and 8.5 using tris buffers (50 mM). The assay mixture contains 500  $\mu$ l of polymer suspension (0.5 mg/ml), 50 mM tris buffer (1.0 ml) and enzyme (500  $\mu$ l). The reaction mixture was stirred after the addition of enzyme and the decrease in turbidity of polymer suspension was measured using optical absorption at 600 nm. The extent of depolymerase activity/

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