

An overview on the degradability of polymer nanocomposites

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Abstract

Polymer nanocomposites have attracted great attention world wide from both academic and industrial points of view. The material properties of polymers can be enhanced dramatically by incorporating layered silicates at fairly low concentrations. The durability of any material depends upon several factors e.g. light, heat, microwaves, mechanical abrasion etc. The study and the effect of these factors on the performance are essentially required to extend the application limits. The durability of polymer nanocomposites has been evaluated under different environments. The present review describes the durability of different polymer nanocomposites mainly under thermal- and photoageing. Biodegradable nanocomposites of different polymers are also discussed briefly.

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Keywords: Nanocomposites; Degradation; Layered silicates; Biodegradation; Weathering

Abbreviations: OMS, organically modified clay; UV, ultra violet; PE, polyethylene; MMT, montmorillonite; OMMT, organically modified montmorillonite; EVA, ethylene–vinyl acetate copolymer; ESO, epoxidised soybean oil; PCL, polycaprolactone; PP-g-MA, polypropylene grafted maleic anhydride; NO_x, nitrous oxide; PA-6, nylon-6; LDPE, low density polyethylene; ATH, aluminium trihydroxide; ODA, octadecylamine; ADA, aminododecanoic acid; VB-16, *N,N*-dimethyl-*n*-hexyl-(4-vinyl benzyl) ammonium chloride; PS, polystyrene; Na-MMT, sodium montmorillonite; PANI, polyaniline; PLA, polylactide; O-PCL, oligomeric polycaprolactone; TPS, thermoplastic starch; WVA, water vapour absorption; TEC, triethyl citrate; BAP, biodegradable aliphatic polyester; PHB, poly(hydroxybutyrate); ELO, epoxidised linseed oil; GPTMS, 3-glycidoxypolytrimethoxysilane; CFRP, carbon fibre reinforced composites; HTA, hydrogenated tallow alkyl; PHA, polyhydroxyalkanoates; PBS, poly(butylene succinate); ESR, electron spin resonance; ESCA, electron spectroscopy for chemical analysis; GC, gas chromatography; GPC, gel permeation chromatography [size exclusion chromatography]; GC–MS, gas chromatography–mass spectroscopy; MALDI-TOF, matrix assisted laser desorption ionisation time-of-flight mass spectrometry; LC, liquid chromatography; DMA, dynamic mechanical analyser; LSC, liquid scintillation counting; SEM, scanning electron microscopy; TEM, tunnelling electron microscopy; XRD, X-ray diffraction; DSC, differential scanning calorimetry; TGA, thermogravimetric analysis.

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1. Introduction

The commercial importance of polymers has been driving intense applications in the form of composites in various fields, such as aerospace, automotive, marine, infrastructure, military etc. [1]. Performance during use is a key feature of any composite material, which decides the real fate of products during use in outdoor applications. Whatever the application, there is often a natural concern regarding the durability of polymeric materials partly because of their useful lifetime, maintenance and replacement. The deterioration of these materials depends on the duration and the extent of interaction with the environment. In recent years it has been found that layered silicate filled polymer composites often exhibit remarkable improvement of mechanical, thermal and physicochemical properties when compared with pure polymer and their conventional microcomposites, even at very low filler concentration due to the nano-level interactions with the polymer matrix [1–4]. These layered silicates have attracted great attention of researchers because of their

low cost, abundance and high aspect ratio, which give greater possibility of energy transfer from one phase to another.

The layered silicates used in the preparation of nanocomposites generally consist of phyllosilicates and more precisely 2:1 phyllosilicate [5]. The clay morphology consists of layers of tetrahedral silicate sheets (Si, Al) and octahedral hydroxide [$\text{Mg}(\text{OH})_2$ or $\text{Al}(\text{OH})_3$] sheets. The tetrahedral sheet consists of individual silica tetrahedra, which shares three out of four oxygen atoms, forming a plane sheet. The sheet composition can be represented as T_2O_5 where T indicates cations of Si and Al and at the same time Fe and B. The octahedral sheets consist of an individual octahedron sharing edges composed of oxygen and hydroxyl with positively charged species Al, Mg, Fe^{+++} and Fe^{++} which serve as coordinating cations. The layer thickness is around 1 nm whereas the lateral dimensions may vary from 300 nm to several microns depending upon the silicate structure.

To ensure the best product from the nanocomposite, either a surfactant/modifier in clay is adequate to offer sufficient excess enthalpy for the promotion of complete and homogenous dispersion of mineral filler in polymer or functionality in the host matrix is usually required. For most non-polar polymers, an alkyl ammonium surfactant is used as modifier for the promotion of complete dispersion of filler into the polymers. Phase separated microcomposites are formed when the polymer is unable to penetrate layers. When one or more extended polymer chains interact with silicates, ordered multilayer morphological composites generate with alternative polymer and clay layers. These composites are called intercalated nanocomposites. If the filler silicate layers are absolutely and homogeneously dispersed in the polymer matrix, the morphology is known as an exfoliated nanocomposites. Recently it was proposed [6] that in the case of LDPE and OMS nanocomposites there may be another state of filler inside the matrix having an ordered exfoliated structure due to the ordering of silicate plates induced by steric interaction. The existence of dual morphologies in intercalated structure explained the effect of an attractive interaction between adjacent layers on the morphology evolution as well as the range of the attractive interaction. A technique to determine the three-dimensional (3D) orientation of various organic and inorganic structures in polymer nanocomposite has recently been developed [7,8], whereas solid-state NMR (^1H and ^{13}C) can also be used for study of the morphology and surface chemistry [9].

The nanocomposites of polymer-layered silicates can be synthesized by the following methods: (i) *Solution method*: organo-modified clay and polymer are dissolved in a polar organic solvent. In general way the linear polymers do not coil in the intergallery space but remain

in almost fully extended state. After solvent evaporation, generally an intercalated nanocomposites may form. (ii) *In situ method or interlamellar polymerisation*: clay is dispersed in the polar monomer solution and after a complete dispersion in monomeric solvent the curing agent is added and generally an exfoliated composite is formed. (iii) *Melt intercalation method*: includes the blending of molten thermoplastic with silicate in order to optimise the interaction. The process may require trial and error based experiments with different compatibilisers. The experimental conditions should be established in order to abolish the coherence of the clay layers. In this process usually the temperature should not increase beyond the decomposition temperature of the clay modifier. The clay minerals might also be synthesized inside the polymer matrix but this process has not been explored like others. Preparation of true nanocomposites is a scientific and technical challenge because fillers must be dispersed in the polymer matrix. In many systems, the chemical nature of the filler is often less important than the particle size and shape, the surface morphology and the extent of distribution within the polymer matrix. Nanocomposites of several polymers have been prepared and studied in detail from the morphological and structural point of view.

In the present review we do not pretend to provide a comprehensive review of the subject of nanocomposite degradation due to the lack of more systematic studies. We will try to address the outline of the current research in the direction of durability of nanocomposites including the discussion of technical problems and their possible solutions.

1.1. Degradability vs. durability

Degradation is a process where the deterioration in the properties of the polymer takes place due to different factors like, light, thermal, mechanical etc. As a consequence of degradation, the resulting smaller fragments do not contribute effectively to the mechanical properties, the article becomes brittle and the life of the material becomes limited. Thus, any polymer or its composite, which is to be used in outdoor applications, must be highly resistant to all environmental conditions. There is a well-established mechanism of polymer degradation as well as their stabilization (Fig. 1). The study of degradation and stabilization of polymers is an extremely important area from the scientific and industrial point of view and a better understanding of polymer degradation will ensure the long life of the product. Not enough attention has been given to the study of durability of thermoplastics as compared to their preparation techniques and evaluation of mechanical properties.

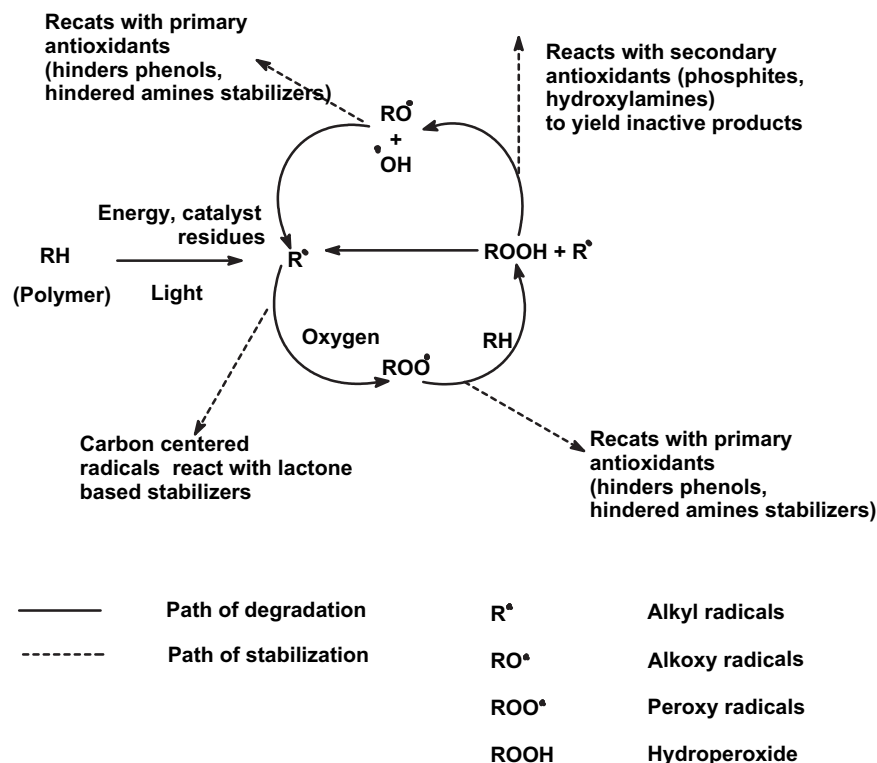


Fig. 1. Different pathways of degradation and stabilization.

1.2. Evaluation methods for durability

The durability of polymeric materials can be studied under several environmental and artificial conditions, which have been summarized in Fig. 2 to avoid an over-long review. The most applicable and popular measurement of photodegradation in thermoplastics is UV irradiation in a weatherometer. This practice provides a procedure for performing outdoor accelerated exposure testing of plastics and is applicable to a range of plastic materials including films, sheets, laminates and extruded and moulded products. This practice describes the test conditions that attempt to stimulate plastics exposures in desert and sub-tropical climates. Polymer samples can also be irradiated in SEPAP 12/24 (from M/s Material Physico Chimique, Neuilly/Marne, France) at 55 ± 5 °C in the presence of air. The unit consists of four 400 W 'Medium Pressure' mercury vapour sources filtered by a Pyrex envelope supplying radiation of wavelength longer than 290 nm. These sources are located at four corners of a square chamber ($\sim 50 \times 50$ cm). The inside wall of the chamber is made up of high reflection aluminium. Two fans on the wall of the chamber are monitored by a Eurotherm device and afford regulation of the temperature of samples (± 2 °C between 50 and 65 °C). The characterization of degradation can be carried out by several means, which are summarized in Fig. 3. Almost all analytical techniques can be used for the evaluation of durability.

2. The durability of nanocomposites from specific polymers

2.1. Polyethylene (PE)

The nanocomposites of PE can be synthesized by in situ polymerisation [10,11], solution blending and melt intercalation [9,12,13]. The nanocomposites exhibit higher heat distortion temperatures, enhanced flame resistance, increased modulus, better barrier properties and decreased thermal expansion coefficient, which may lead to applications in the automobile industry and to lightweight, high temperature applications such as aircraft. Many researchers studied the degradation of PE, but the degradation behaviour of PE nanocomposites is not well studied. The environmental degradation of thermoplastic nanocomposites has been evaluated under UV irradiation and in biotic environments [14]. Nanocomposites showed higher degradability than controlled samples. It was assumed that, once oxygen reached the matrix, it will remain for longer time because clay will interfere in the path thus O_2 is easily available for longer time to initiate the degradation faster than for the neat polymer. Huaili et al. [15] studied the photo-oxidative degradation of PE/MMT nanocomposites compared with neat polyethylene. The intercalated PE-OMMT nanocomposites were prepared by using twin-screw extruder. The films were exposed to UV radiation under oxygen atmosphere. It is

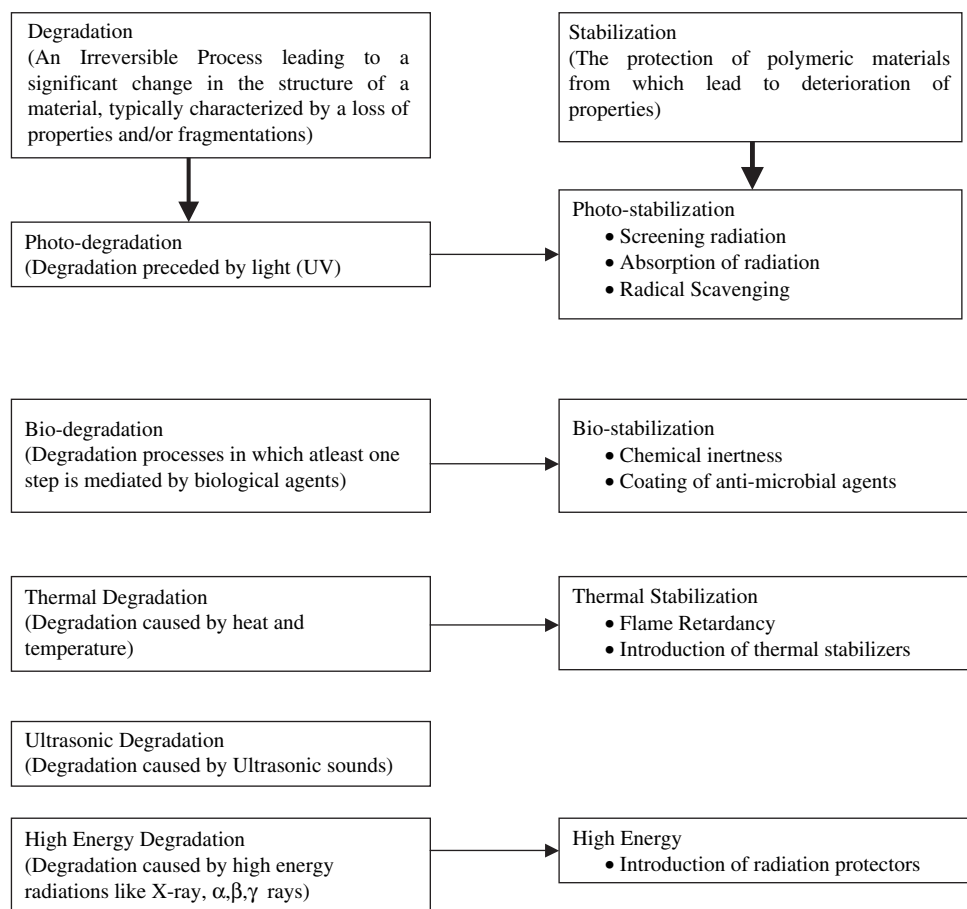


Fig. 2. Schematic representation of different degradation and stabilization processes in polymers.

well-established that the degradation of hydrocarbon chains lead to the formation of hydroxyl and keto groups. From Fig. 4 we can clearly see that the degradation of the PE/OMMT nanocomposite was more than the pure PE polymer after 200 h irradiation. Fig. 5 shows the FT-IR spectra in the carbonyl region upon UV irradiation. It shows that there is considerable increase in the intensity of the carbonyl region as increase of irradiation time in the PE/OMMT, which means that material is undergoing degradation. But in the pure PE the intensity in the carbonyl region was significantly less, which shows less degradation.

Zanetti et al. [16] studied the thermal degradation of PE/OMMT clay nanocomposite. The nanocomposites were made by melt compounding in the Brabender. The degradation of PE/EVA/MTC18, PE/MTC18, and PE/EVA were studied in the presence of nitrogen and air. Here EVA is used as a compatibiliser. It was observed that the difference in decomposition temperatures was not much in nitrogen atmosphere. In the degradation of neat PE/EVA, deacylation of acetate groups occurs at 350 °C whereas in PE/EVA/MTC18 nanocomposites deacylation occurs at 280 °C. The thermal degradation of nanocomposites is less than that of pure polymer in

the presence of air. The effect of clay dispersion on the degradation of nanocomposites was not understood in detail. The degradation mechanism and degraded products are yet to be studied.

2.2. Polypropylene (PP)

PP has a wide range of applications such as packaging, fibres, automobile industry, non-durable goods and in building construction. There are several reports of success in the synthesis of PP nanocomposites by different methods [17–21]. Very few efforts have been made on the degradation behaviour of PP nanocomposites. Morlat [22] and Mailhot et al. [23] studied the effect of compatibilisers on photo-degradation and its kinetics by comparing nanocomposites with neat polymer. The increase in the absorbance at 3200–3600 cm^{-1} and 1600–1800 cm^{-1} was rapid in nanocomposites in comparison to neat polymer. It was observed that the induction period decreased from 8 to 4 h by using PP-g-MA as compatibiliser and two-phase degradation mechanism was observed. In the first phase (up to 40 h) there was no evidence for the hydroxyl band formation in the IR spectra, which implied the absence

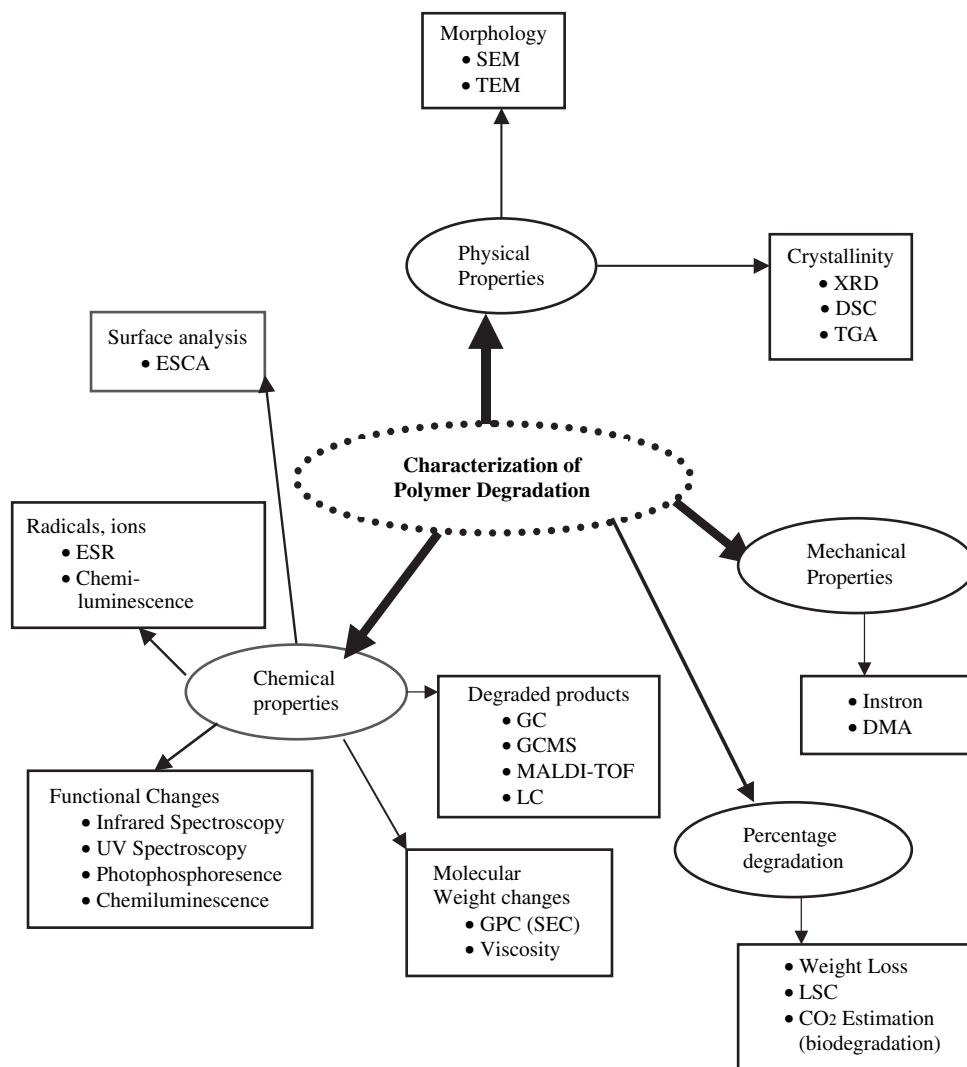


Fig. 3. Different analytical techniques to analyze the polymer durability.

of degradation on polymer backbone, whereas in the second phase dramatic increase in the rate of photo-oxidation was found. The degradation products were same in the composite as well as the neat polymer. Zanetti et al. [24] studied the thermo-oxidative degradation of PP/OMMT nanocomposites by using TGA. They found that the nanocomposites were more stable ($> 50\text{ }^{\circ}\text{C}$) in comparison to neat polymer and they proposed a mechanism. As shown in Fig. 6 oxygen will attack at the carbon radical within the chain by H abstraction. Around $200\text{--}250\text{ }^{\circ}\text{C}$ hydrogen abstraction becomes more likely as shown in process B, thus resulting in oxidative dehydrogenation. As the temperature increases, the concentration of chain end radicals (e.g. II) increases because beta scission of radicals I (process C) becomes competitive with either oxygen addition (process A) or hydrogen abstraction (process B). Direct thermal scission of carbon–carbon bonds becomes possible above $300\text{ }^{\circ}\text{C}$.

2.3. Polycarbonate (PC)

PC is bisphenol-A based polyester, which is an important engineering thermoplastic having unique properties like transparency, toughness, thermal stability and dimensional stability. These properties gave it uses in many applications like compact discs, riot shields, vandal-proof glazing, baby feeding bottles, electrical components, safety helmets and headlamp lenses. Very few efforts have been made in the synthesis of polycarbonate nanocomposites [25] and few efforts have been made for degradation of polycarbonate nanocomposites. In polycarbonate degradation carbonate linkages undergo a scission reaction upon UV exposure. The incorporation of the layered silicates appears to increase the rate at which chain scission occurs. Furthermore, these carbonate scissions produced a yellowing of the polycarbonate which can inhibit its use in applications where optical clarity is

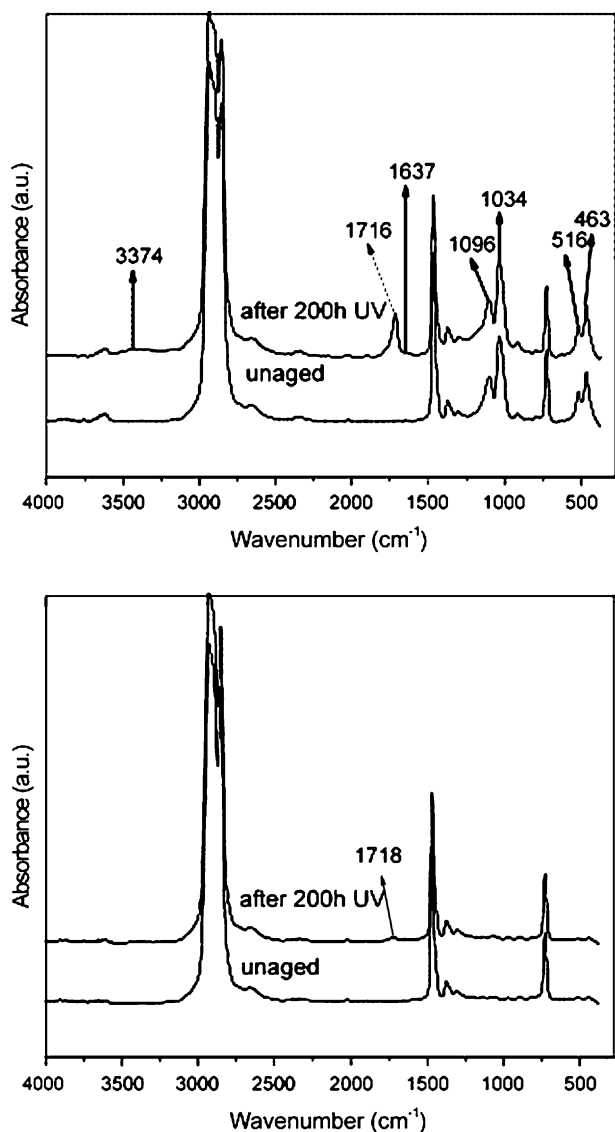


Fig. 4. (a) FT-IR spectra of PE/OMMT nanocomposites before and after 200 h irradiation. (b) FT-IR spectra of pure PE before and after 200 h UV irradiation. (Reproduced with permission from Huaili et al. [15].)

important [26]. In this study, the effect of accelerated weathering of polycarbonate nanocomposites was investigated [27]. The silicate content used ranged from 0 to 3.5 wt.%. A UV-accelerated weathering tester programmed to cycle for 8 h of UV radiation and 4 h of dark condensation was selected for the exposure study. The materials were characterized by UV/vis spectroscopy and FT-IR spectroscopy. Here it was concluded that the degradation of the nanocomposite was less as compared to the neat polymer.

2.4. Nylon

Nylon is an engineering thermoplastic, commercially made by anionic ring opening polymerisation of

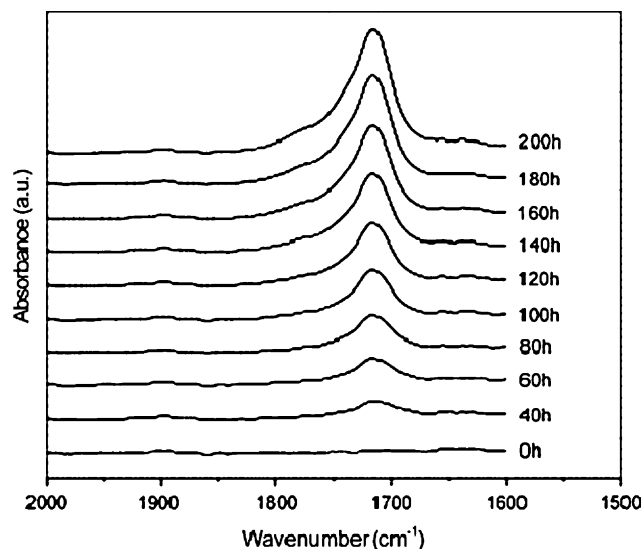


Fig. 5. FT-IR spectra of PE/nanocomposite at carbonyl region during photodegradation. (Reproduced with permission from Huaili et al. [15].)

caprolactam and is used in filaments of toothbrushes, ropes and filaments for garments like raincoats and is also used in the automobile industry for self-lubricating gears and bearings. Nylons were the first commercial polymer nanocomposites made by Toyota research group [28] and were prepared by typical methods [29,30]. These nanocomposites are mainly used in the automotive and packaging industries thus the durability has been widely investigated. The thermal degradation mechanism of PA-6 has been proposed by Levchik et al. [31] as in Fig. 7. Vander Hart et al. [32] observed that in the presence of clay the α -phase of nylon-6 transforms into the γ -phase. The effect of modifier on the degradation of nanocomposite was studied by ^{13}C NMR. In the presence of modifier (dihydrogenated-tallow ammonium ion) the nylon nanocomposite begins to degrade at 240 °C, whereas the virgin polymer does not. They concluded that the organic modifier is less stable. The combination of shear stress and temperature may lead to extensive degradation of the modifier and the extent of clay dispersion may not depend on the modifier. Recently Davis et al. [33] have studied the thermal stability of injection moulded PA-6 nanocomposites by ^{13}C NMR. The virgin PA-6 and its nanocomposites were injection moulded at 300 °C. PA-6 does not degrade at processing temperature, whereas there is significant decrease in molecular weight in nanocomposites in the same conditions. It was observed that the degradation might depend upon the percentage of water in the nanocomposites, which might cause hydrolytic cleavage.

Fornes et al. [34] found colour formation with polymer matrix degradation after twin-screw extrusion of nanocomposites. The degradation of the nanocomposite

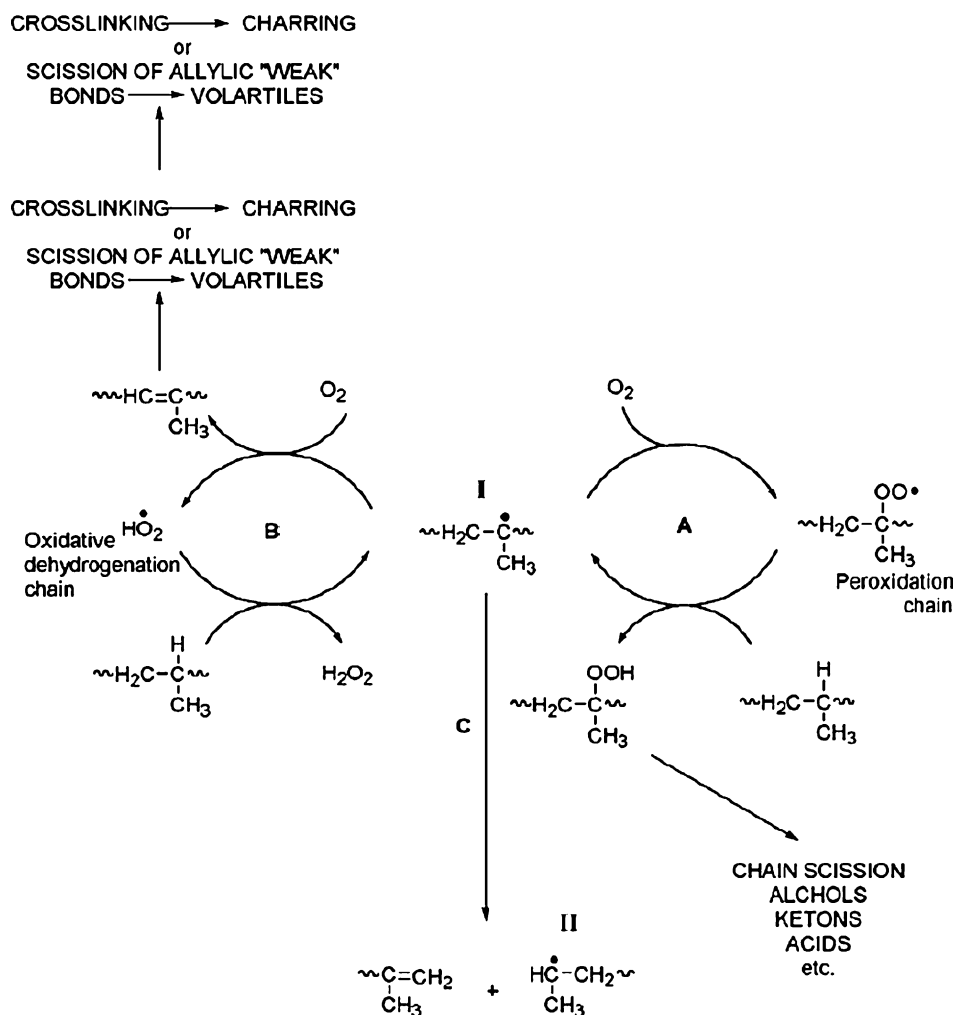


Fig. 6. Thermal degradation mechanism of PP nanocomposites. (Reproduced with permission from Zanetti et al. [24].)

depends on the type of nylon-6 materials as well as the chemical structure of the surfactant in the OMMT (Fig. 8). For a given organoclay, the level of polymer molecular weight reduction and deepness of colour were found to be greatest for nanocomposites based on high molecular weight nylon-6 materials; this has been attributed to more exposure of the surfactant to the nylon-6, owing to increased levels of organoclay exfoliation. Hydroxy-ethyl groups in the surfactant, as opposed to methyl groups, and tallow substituents, as opposed to hydrogenated tallow substituents, produce more colour in nanocomposite which was related to unsaturation in the alkyl ammonium surfactant causing considerable polymer degradation. The kinetic parameters of PA-6 clay nanocomposite decomposition have also been studied; where a diffusion process seems to control the thermal degradation [35].

Pramoda et al. [36] observed that the temperature of onset of degradation for nylon-6 and 2.5% clay filled nanocomposites was higher than other compositions

[neat polymer, 5% and 7.5%, respectively]. Gilman et al. [37] proposed that with the higher loading of clay, temperatures of onset of degradation remain unchanged, which was attributed to agglomeration in nanocomposites. The presence of organoclay [for PA6 – 2.5 wt.% clay nanocomposite] increased the activation energy for degradation, E_a , compared to the neat PA-6 under N_2 . The major evolved gas products were cyclic monomers, hydrocarbons, CO_2 , CO , NH_3 and H_2O for PA-6 and PA-6-clay nanocomposites.

Shelley et al. [38] have found that NO_x gases have adverse effects on the mechanical properties. NO_x is known to cause rapid chain scission – apparently there is decrease in molecular weight with exposure time in nylon-6. NO_x attacks the nylon polymer chain, deprotonating the amide nitrogen and ultimately causing the chain scission at the weakest C–N bond. As in the nylon-6 clay nanocomposites, the nylon polymer chains and silicate layers are oriented in the direction of flow and the diffusion is controlled with orientation [39], the

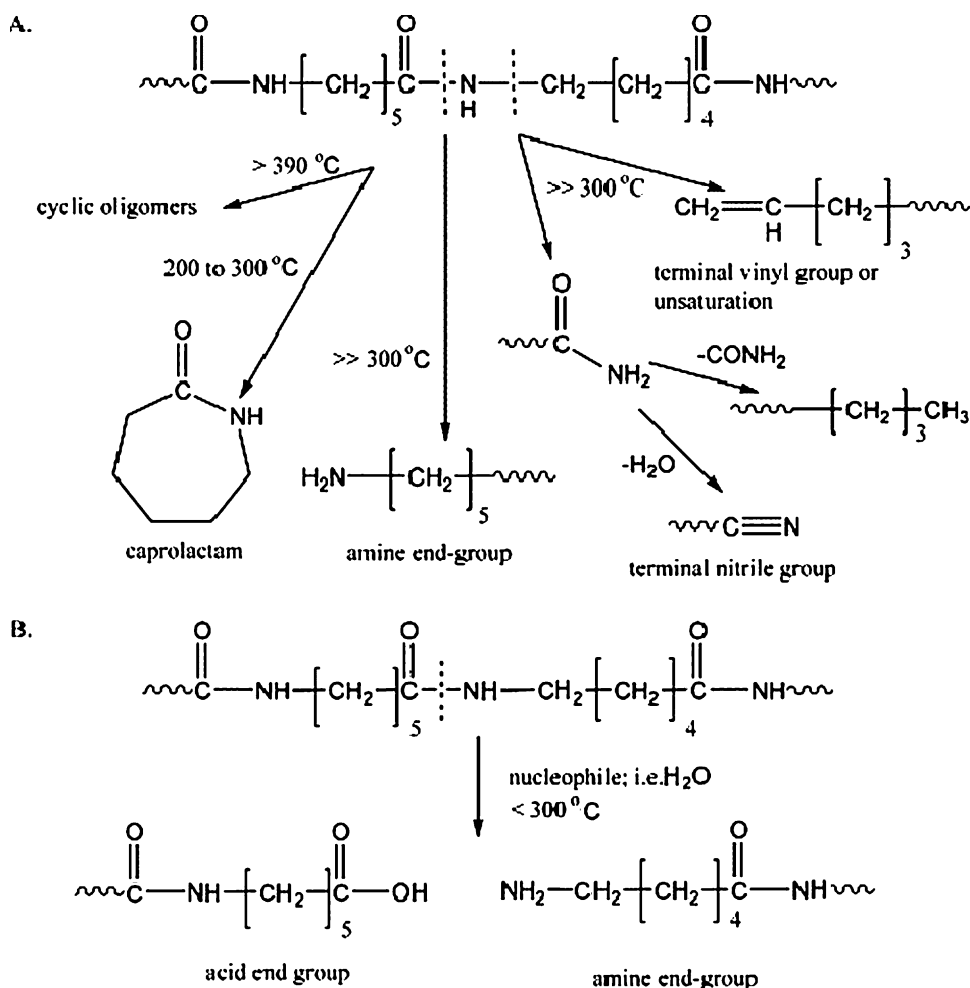


Fig. 7. Dominant PA-6 thermal degradation products in the absence of a nucleophile (A) and in the presence of a nucleophile, such as water (B). (Reproduced with permission from Davis et al. [33].)

strength decayed logarithmically with exposure time and linearly with concentration. It was believed that the tacky layer formation on the surface of the film was more severe with increasing time. According to Fuchs [40], nitric acid is a solvent for nylon-3, but the solvation interrupts the inter-chain hydrogen bonding and dissociates the molecules from one another, leading to a stress cracking response. However, all the three mechanisms, NO_2 attack, hydrolysis, and solvation, influence the mechanical response of the nylon-6 and its nanocomposites. In addition, the constraining effect of the silicate layers was not found to protect the nanocomposite materials from NO_x attack.

2.5. Poly(vinyl chloride) (PVC)

PVC has high chemical and abrasion resistance, and is widely used in durable applications, e.g. for pipes, window profiles, house siding, wire cable insulation and flooring. The structural defects and isomeric forms

resulting from radical polymerisation can induce thermal instability of PVC during use, because thermal dehydrochlorination of PVC often begins with internal allylic chloride and tertiary chloride in the main chain [41]. Few publications about preparation and degradation of PVC/clay nanocomposites have been reported and the fine nanostructures of resultant nanocomposites are scarcely obtained [42–44]. Recently Du et al. [45] have found, in their degradation study of PVC nanocomposites using XPS, that carbon intensity at the surface was increased which is contrary to the results obtained for PMMA [46] and PS [47]. This was attributed to the degradation pathway of PVC which is quite different from PMMA and PS [48]. In case of other polymer nanocomposites, the polymer is lost and clay accumulates on the surface but for the PVC nanocomposites, the polymer forms a carbonaceous char. It is believed that the compatibiliser/plasticiser also has influence on the degradation of nanocomposites because of its loss at higher temperatures (350 °C). For

HMW Nylon 6 Nanocomposite	% MMT	L*	Photograph of ASTM Tensile Bar ^(a)
Virgin	0.0	53.6	
Extruded	0.0	56.8	
(HE) ₂ M ₁ R ₁	3.2	41.7	
(HE) ₂ M ₁ C*	2.9	48.9	
(HE) ₂ M ₁ T ₁	2.8	45.3	
M ₃ T ₁	2.8	48.6	
M ₃ (HT) ₁	2.9	49.6	

(a) Photographs were taken on 3.18 mm thick specimens.

Fig. 8. The effect of organoclay structure on color formation in high molecular weight nylon-6 nanocomposites. Where (HE)₂M₁R₁ – bis(2-hydroxy-ethyl)methyl rapeseed ammonium montmorillonite; (HE)₂M₁C* – bis(2-hydroxy-ethyl)methyl coco ammonium montmorillonite; (HE)₂M₁T₁ – bis(2-hydroxy-ethyl)methyl tallow ammonium montmorillonite; M₃T₁ – trimethyl tallow quaternary ammonium montmorillonite; M₃(HT)₁ – trimethyl hydrogenated-tallow ammonium montmorillonite. (Reproduced with permission from Fornes et al. [34].)

enhanced thermal stability, they believed that the presence of clay stabilizes the allylic species, which formed during degradation.

Then latest studies on the thermal stability [49] have also shown that clay incorporation into PVC enhances the rapid decomposition and reduces the maximum decomposition rate and the temperature of onset of decomposition. A compact char structure formation with plenty of carbonaceous MMT on the surface of the nanocomposites, obstructing the thermal degradation of the polymer matrix at high temperature as seen in the XPS study. The presence of the quaternary ammonium in the nanocomposites is responsible for the acceleration of the polymer decomposition in the initial stage.

2.6. Ethylene-co-vinyl acetate (EVA)

Ethylene–vinyl acetate copolymer (EVA) is a widely used material, particularly as a zero-halogen material in the cable industry. It is frequently formulated with large quantities of inorganic filler material, such as aluminium trihydroxide (ATH). Since the nanoclay incorporation is also believed to assist the formation of a protective layer, researchers have studied the decomposition behaviour of EVA nanocomposite using nanofillers [50,51]. According to Hull et al. [50] incorporation of clay reduced the rate of decomposition significantly. Thermal degradation of EVA occurred in two stages, in the first acetic acid was lost and in the second cross-linking took place. There is significant improvement in flame retardancy even though clay is not dispersed

properly, which suggests that the clay particles are able to reinforce the protective layer formed. The combustion behaviour of EVA nanocomposites based on ODA and ADA modified fluorohectorite is found to be similar to that in thermal decomposition [51]. A delayed heat release results from delayed evolution of degradation products combined with the barrier effect of dispersed nanolayers. Furthermore, the nanocomposite provides physical integrity to the material burning in configurations (e.g. vertical upward combustion) in which fire dripping of flamed material could occur which represents an additional hazard due to fire propagation to surrounding materials.

2.7. Poly(methyl methacrylate) (PMMA)

Poly(methyl methacrylate) (PMMA) is widely used in adhesives, automotive signal lights, lenses, light fittings, medallions, neon signs and protective coatings because of the excellent, optical (clarity), physical and mechanical (dimensional stability with high modulus) properties. PMMA nanocomposites can be prepared for enhancing the above-mentioned properties [52,53]. Their durability is of paramount importance because of their applications in different fields. Du et al. [46,54] studied the thermal degradation of PMMA nanocomposites by analyzing the surface through XPS. As soon as the temperature is increased carbon is lost from the surface of PMMA nanocomposites and oxygen accumulation starts. On thermal degradation of the neat polymer and conventional composites, carbon intensity was found to increase. But in the nanocomposite, silicon and oxygen try to move to the surface. It is well known that the ammonium cations undergo thermal degradation (Hoffman degradation) in the temperature range 200–300 °C. This leads to the complete loss of the cation and its replacement with a proton as the counter ion of the clay. Since this change in silicon: aluminium ratio occurs in the same temperature region, it is a reason to suppose that the loss of the cation may have some effect on the structure of the clay, ultimately on the polymer degradation.

2.8. Polystyrene (PS)

PS is a strong plastic, that can easily be injected, extruded or blow moulded for making it a very useful and versatile manufacturing material. The nanocomposites of PS can be prepared by several routes like in situ polymerisation [55], bulk polymerisation [56], solution blending [57] and melt blending [58–60], but very few efforts have been made to understand the degradation behaviour of PS nanocomposites. Vyazovkin et al. [61] studied the kinetics of the thermal and thermo-oxidative degradation of PS nanocomposite. The thermal

degradation of the nanocomposite was compared with virgin polymer under nitrogen and air. The virgin polymer degrades without forming any residue, whereas the nanocomposite leaves some residue. As seen in Fig. 9 in both nitrogen and air the decomposition temperature of nanocomposites increases by 30–40 °C whatever the atmosphere. It was concluded that the introduction of clay into PS, considerably increases the thermal stability. Bourbigot et al. [62] analyzed the kinetics of thermal degradation of PS nanocomposite. The clay used in this attempt was modified with VB-16 and nanocomposites were synthesized by in situ bulk polymerisation. In TGA studies (about 200 °C), in the case of nanocomposites initially less weight loss was observed which could be attributed to the degradation of organo-modifier of clay. The onset of thermal degradation of PS nanocomposite was 50 °C higher than that of the virgin PS, whereas in thermo-oxidative degradation there was not much difference. The kinetic studies showed that the mechanism of the nanocomposite differs from virgin polymer.

Zhang and Wilkie [63] studied a novel carbocation (tropylium) as a clay modifier and its thermal stability. They compared the stability of clay with neat, ammonium and organically modified clays. The PS nanocomposites were made via in situ polymerisation. It was observed that the stability of styryltropylium clay is more than the ammonium clay. The initial decomposition temperatures were 15–27 °C, more than the virgin polymer. The overall conclusion is that, the PS nanocomposite has less thermal and thermo-oxidative

stability than its virgin polymer. The photo-stability of the PS nanocomposite is yet to be studied.

2.9. Natural rubbers/ethylene–propylene diene monomer (EPDM)

Vulcanized rubbers are usually reinforced by carbon black and also by inorganic minerals (talc, TiO₂, etc.) to improve the mechanical properties. Carbon black is an excellent reinforcement owing to its strong interaction with rubbers, but its presence, especially at high loading, often decreases the processability of rubber compounds. Commercial clay has been used as filler for rubber for many years. On the other hand, minerals have a variety of shapes suitable for reinforcement [64–66], such as fibrils and platelets. The thermal decomposition behaviour of NR nanocomposites [66] was studied. At 400 °C, the percentage of weight retained is higher for the nanocomposites. In our recent studies [67] photodegradability of EPDM nanocomposites, prepared by melt blending with cloisite 20 A, were examined under UV light. The nanocomposites generated same degradation products as in neat EPDM at faster rate. Degradability was increased with the filler concentration in the matrix. The modifier played key role during degradation under UV light whereas the exact mechanisms are not understood well.

2.10. Polyaniline

Polyaniline (PANI) is a conducting polymer and its properties are strongly dependent on synthetic procedures, type of dopant, morphology, and other variables. PANI-inorganic nanocomposites have also been proven to possess a wide range of properties such as electrical, mechanical, and structural properties because of synergistic effect owing to the intimate mixing between organic components in molecular level [68]. Kim et al. [69] have reported first the synthesis of nanocomposite based on layered silicates, and more reports have been made on the synthesis of the smectite clay-nanocomposite and their properties improvement [70]. The degradation behaviour of polyaniline nanocomposite is yet to be clearly understood. Lee and Char [71] have found that the Na-MMT/PANI nanocomposites were more thermally stable than the physical mixture of Na-MMT and PANI. Polyaniline undergoes a three-step thermal decomposition. The weight loss in the third step, which is attributed to polyaniline backbone decomposition, was found to be maximum at 530.6 °C for pure PANI and this was shifted 25 °C more for Na-MMT/PANI nanocomposite. From the XRD investigation after TGA analysis, it can be concluded that the PANI chains residing outside the silicate layers decomposed mostly and inside the chain residing layers to a small extent. So the shielding effect of intercalation into the

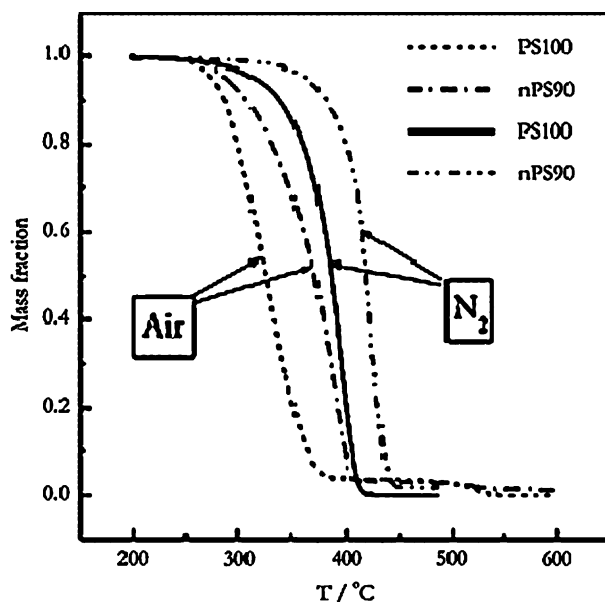


Fig. 9. TGA curves of the degradation of PS100 and nPS90 at a heating rate 5 °C min⁻¹ in air and nitrogen. (Reproduced with permission from Vyazovkin et al. [61].)

layers imparts the thermal stability to polymeric materials.

2.11. Epoxy resins

The synthesis of epoxy-based nanocomposites has been reported with different epoxy monomers [72–74]. The thermal stability of the epoxy nanocomposites is being explored [75–77]. According to the recent investigation [78], the thermal degradation of nanocomposites depends on the clay loading, and structure and the nature of the ambient gas. A nanocomposite with 2 wt.% loading showed one step degradation, whereas 10 wt.% clay loading showed two steps and the maxima of degradation were at 395 °C and 397 °C, indicating that degradation started at lower temperature with increasing loading of clay. There are two factors which have opposite influences on the thermal stability of epoxy–clay nanocomposites. First factor according to Deng [79] is that the addition of clay to epoxy decreases the curing reactivity of epoxy resin. Lower reactivity of the resin generally results in lower cross-linking density of the cured resin and the longer polymer chains among the cross-linking points. It is known that a longer polymer chain is less stable thermally than a shorter chain, so both the nanocomposites are easier to degrade than the pristine epoxy resin. Secondly, silicate layers have good barrier to gases such as oxygen and nitrogen, they can insulate the underlying materials and slow the mass loss rate of decomposition products. Moreover, exfoliated nanocomposites have better barrier properties and thermal stability than intercalated ones [80]. In the case of intercalated nanocomposites (10 wt.% clay), the first factor is dominant, whereas for an exfoliated nanocomposites (2 wt.% clay), the second factor is dominant. Becker et al. [81] have found that the water uptake (in aquatic environment) was considerably

reduced in epoxy nanocomposites with a particular clay loading percentage.

2.12. Nanocomposites of biodegradable polymers

2.12.1. Polylactide (PLA)

PLA is a linear thermoplastic polyester produced from renewable resources. The ester bonds are prone to both chemical and enzymatic hydrolysis. Since some properties like melt viscosity, impact factor, heat distortion temperature, gas barrier etc. are not good enough for its use in various applications, efforts have been made in this direction. The layered silicate PLA nanocomposites were prepared not only to increase its mechanical properties but also for enhancement of barrier properties. Many authors [82–93] have prepared nanocomposites of PLA and studied several properties including biodegradability in composting. The nanocomposites were prepared by melt intercalation method [94] by using O-PCL as compatibiliser. During biodegradability testing of these nanocomposites in industrial compost, an increased biodegradation was evidenced as samples were completely mineralised after 60 days (Fig. 10). It was expected that the presence of terminal hydroxylated edge groups of the silicate layers might be one of the factors responsible for this behaviour [95]. In the case of 4% filler content the silicate layers were homogeneously dispersed in the PLA matrix and these hydroxy groups start heterogeneous hydrolysis of the PLA matrix after absorbing water from compost. Since this process may take some time, the weight loss and degree of hydrolysis of PLA and PLA with 4% filler is almost same up to one month and after that nanocomposites degraded faster and one month of composting was found to be a critical time for degradation rate.

Lee et al. [96] prepared aliphatic unsaturated polyester [copolymer prepared by polycondensation of

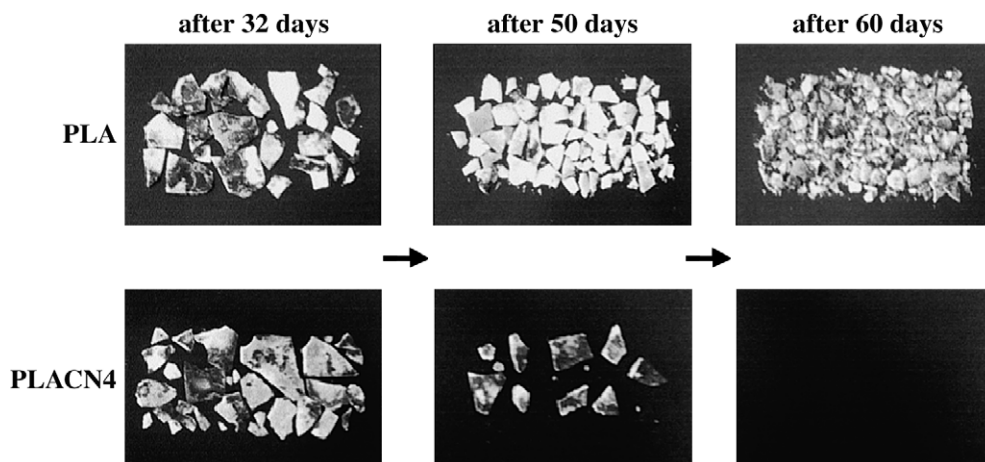


Fig. 10. Photographs of composites during degradation while composting. (Reproduced with permission from Ray et al. [95].)

aliphatic glycols (ethylene glycol and 1,4-butane diol) with succinic and adipic acids having MW of 60,000] clay nanocomposites by melt intercalation. This article reported the decrease in biodegradability under composting with intercalation and it was concluded that due to high aspect ratio and better dispersion of clay in matrix a more tortuous path formed for microorganism penetration inside the bulk and hindered their diffusion.

Moreover the decrease or increase in biodegradation in nanocomposites is under discussion and no conclusion can be made about their mechanisms on the basis of present literature. Dubois et al. [97] prepared PLA layered silicate nanocomposites by melt intercalation in the presence of a stabilizer to decrease the possibility of host matrix degradation due to heating. The degradation of PLA during processing takes place even in the presence of antioxidant, and 41.2% decrease in number average molecular weight was observed compared to native PLA. An increase in the thermal stability under oxidative conditions was found and it was suggested that a physical barrier between the polymer medium and superficial zone of flame combustion may be generated due to the char formation. The adoption of PLA for automotive parts has been studied in order to contribute to suppressing the increase in CO₂ emissions [98]. For this application, major improvements of heat and impact resistance are needed. It was found that in-mould crystallization of the PLA–clay nanocomposite led to a large suppression of storage modulus decrease at high temperature, which in turn improved the heat resistance of PLA.

2.12.2. Starch

The mixing of biopolymers in the matrix of thermoplastics [99–101] has been recognized as a way to get rid of plastic waste. This blending usually leads a phase separation and reduction in mechanical properties due to the lack of compatibility between hydrophilic biopolymer and generally hydrophobic thermoplastic, therefore, in the resulting product, consumption of natural biomaterial by microbes takes place, leaving behind fragmented thermoplastic matrix. A first insight of thermoplastic starch and kaolin clay interaction was reported by Curvelo et al. [102]. Starch, plasticiser (w/w 30%) and clay were mixed in a polyethylene bag till the formation of powder. During TG analysis the residual weight was proportional to the filler content in the matrix. In the same direction biodegradable thermoplastic hybrid was prepared by melt intercalation method [103,104]. It was assumed that there is possibility of controlling the degradation rate of the nanocomposites by varying the filler content as hydrolysis of polymer is possibly dependent on the transport of water from the surface to bulk and this transportation can be controlled by altering the filler content in the system. Degradation studies were not carried out. The

higher thermal stability of intercalated composites was attributed to the better dispersion of clay as the temperature for which the 50% weight loss takes place shifted from 305 to 336 °C for 5% filler content. Wilhelm et al. [105] prepared nanocomposites of starch and concluded that there is no significant effect of clay on the thermal degradation of starch, whereas a significant increase in thermal stability was observed when nanocomposites of thermoplastic starch and unmodified MMT was prepared by melt intercalation method even at 5% filler content [106]. Thus, the preparation method might have an effect on the properties; here it must be recalled that both systems have different class of clays. Composites have been prepared by solution method [107] after drying of starch and clay at 110 °C. All composites show highest weight loss at 296 °C. It was assumed that thermal degradation was influenced by hydroxyl group exposure, clay dispersion and reassociation of starch chains where clay dispersion was more important than others. The plasticisation effect has been studied in starch layered silicate nanocomposites [108]. The direct degradation study of starch nanocomposites have not been done so far and thus there is no experimental explanation about the effect of clay on the microbial consumption of starch.

2.12.3. Cellulose

Cellulose occurs naturally in the crystalline state in plant cell-wall and is isolated as microfibrils by convenient extraction methods. It is made up of β D-(+) glucose residues, and has been widely used for the reinforcement of polymers. Fibres of cellulose of nano-dimensions, called cellulose whiskers, have been successfully used for polymer matrix reinforcement. Biodegradable nanocomposites of cellulose and its derivatives have been prepared [117–120]. Nanocomposites of cellulose acetate, TEC, plasticiser and OMS clay were prepared and different mechanical properties were studied. While examination of WVA a dramatic lowering was observed which was attributed to the large aspect ratio of silicate layers in the polymer matrix as has been observed for other nanocomposites [121,122]. When starch was filled with cellulose whiskers a decrease in water sensitivity and increase in thermo-mechanical properties was observed [109]. Cylindrical microcrystals of cellulose were prepared from a sea animal (tunicate) and films were prepared of different compositions. A higher thermal degradation of the starch matrix was reported for increasing moisture content. There are several reports [110–116] on the reinforcement of biopolymers by biopolymers those may be referred for the further details. In broad sense, the starch and cellulose whisker based bio-nanocomposites may be used as a biodegradable commodity material if we could incorporate more moisture resistance with mechanical

properties. No biodegradability test has been reported on these types of nanocomposites.

2.12.4. Poly(*caprolactone*) (PCL)

In the family of synthetic biodegradable polymers, PCL, which is linear, hydrophobic and partially crystalline polyester, is a biodegradable polymer that can be slowly consumed by microorganisms [123]. Its physical properties and commercial availability make it very attractive not only as a substitute for non-biodegradable polymers of commodity applications but also as a specific plastic of medicine and agricultural areas [124,125]. The main limitation of PCL is its low melting temperature ($T_m \sim 65^\circ\text{C}$), which can be overcome by blending it with other polymers [126]. There have been few attempts to develop nanocomposites of PCL with layered silicates for the improvement in material properties [127,128]. For the first time [129] polymer/clay nanocomposite with synthetic BAP and OMS was prepared by a solvent-casting method. The increase in degradation rate with increasing amount of dispersed clay was observed in the TGA. The domain of polymer and clay nanocomposites could hold accumulated heat which may accelerate the decomposition process. The authors suggested more study for the explanation of this reverse trend in nanocomposites. Dubois et al. [130] prepared PCL nanocomposites by melt intercalation with or without modified clays at 130°C for 30 min in two roll mill. Already reported PCL nanocomposites [131] with 12-dodecanoic acid modified clay via in situ polymerisation could not be reproduced when the same composition was repeated via melt intercalation. Thus, the intercalation/exfoliation of the same composition is dependent not only on preparation route but also on the type and localization of modified groups in clays. It was assumed that even if a given organo-modifier layered silicate can intercalate a monomer with the formation of an intercalated and/or exfoliated composites upon polymerisation, it does not assure that nanocomposites may be generated by direct blending of the corresponding polymer and same modified clay. The nanocomposites showed an improved thermal stability, which is consistent with an effective barrier against permeation of molecular oxygen and evolved combustion gas formed by the silicate sheets. The weight loss due to the formation of volatile degradation products was monitored as a function of temperature. Flame retardancy was remarkable and related to the deposition of an insulating and incombustible char whenever the PCL nanocomposites are exposed to the flame. The detailed study of PCL melt-intercalated nanocomposites with natural Na^+ MMT and HTA based quaternary ammonium cations was conducted by the same author [132]. The nanocomposites were found to be stable and burned without droplets during visual burning examination.

The biodegradability of PCL based nanocomposites was studied under composting conditions after preparation by in situ polymerisation and extrusion [133]. The composites filled with 10% clay showed highest modulus but a decrease in elongation was observed. Biodegradation studies were carried out under soil and marine environments by measuring the evolved carbon dioxide and weight loss, respectively. The data at the incubation of 22°C have a minimal weight loss for both pure PCL and PCL/clay (50/50%) composites in absence of any nutrients of exposure. PCL clay nanocomposites were obtained by melt blending of PCL [134] with OMS and from in situ ring opening polymerisation of caprolactone with OMS. In the TGA it was observed that the clays alone can undergo degradation in two steps, a Hofmann elimination, giving a trialkylammonium cation, followed by the loss of the amine leaving only a proton as the counter ion. The detailed investigation on the biodegradation of PCL nanocomposites is required to conclude the role of modifier, clay dispersion on the mechanism of bioconsumption.

2.12.5. Polyhydroxyalkanoates (PHA)

PHA represents a range of polymers obtained from renewable resources by bacterial fermentation and a wide range of microbes have shown the capability to generate this polymer. This class includes the 3-hydroxybutyrate-*co*-3-hydroxyvalerate polymers marketed under the Biopol trademark [135]. This copolymer is semicrystalline with melting temperature from 120 to 180°C depending on the composition. The strength of this plastic and its crystalline nature usually limit its application as a traditional material. The polymers of this class were confined in layered silicate by assuming that the layered silicates will improve many material properties. An effort has been made in this direction with little explanation of the reaction conditions and properties. Degradation of PHB matrix during nanocomposite preparation was higher in MMT than fluomicas. Degradation rate was checked in nanocomposites in the presence of clay particle. The higher degradation rate in MMT polymer was attributed to the presence of aluminium Lewis acid sites, which catalyse the hydrolysis of the ester linkages [136]. The enhanced barrier properties are believed to decrease the biodegradation by enhancing the path length, as the rate after three weeks is much slower from that of PHB. Cellulose nanowhiskers have been used to reinforce PHB, where a structural and morphological study was carried out with different load concentrations. The preparation of a latex of poly(β -hydroxyoctanoate (PHO) obtained from *Pseudomonas oleovorans* grown at high cell density on sodium octanoate was investigated [137] and a latex was obtained from *P. oleovorans* grown at high cell density on sodium octanoate. Nanocomposite materials were also prepared from

medium-chain-length poly(hydroxyalkanoate) (Mcl-PHA) latex [138] as semicrystalline matrix using a colloidal suspension of hydrolysed cellulose whiskers as natural and biodegradable filler. In both above-mentioned attempts, the study of degradability was not performed. The reinforcement of PHB matrixes may be carried out successfully but the real material properties preservation as in engineering thermoplastics is still an unresolved area of research.

2.12.6. Poly(butylene succinate) (PBS)

The biodegradable nanocomposites have been synthesized from PBS [139] and study on mechanical properties was carried out [140] with the detailed explanation of relation between structure and properties [141]. The material was very much fractured which may have an advantage for biodegradation because of easy mixing with compost and the creation of high surface area for further attack by microorganisms, and it should be noted here that the extent of fragmentation is directly related to the nature of OMS used for nanocomposite preparation. These nanocomposites were found easily biodegradable.

2.12.7. Natural oils

Biodegradable nanocomposites have also been developed from natural oils like epoxidized soya oil that has been used as monomer for production of resins. These vegetable oils have their own particular advantages e.g. they are renewable products derived from natural oils and fats and are more readily biodegradable than the corresponding products made from petroleum sources. Hence their impact on the environment is less. The long fatty acid chains of vegetable oils impart desirable flexibility and toughness to otherwise brittle resin systems such as epoxy, urethane and polyester resins. This oil can be successfully polymerised photochemically in the presence of initiators under defined conditions [142]. Epoxy-exfoliated clay nanocomposites were prepared using [143] long-chain alkylammonium-exchanged smectite clay. The ESO composites were compared with hybrids obtained from ELO those were prepared by similar method. Biodegradability testing has also been carried out on these nanocomposites for the first time and samples were found biodegradable in initial studies [144]. Biodegradable nanocomposites were obtained by plant oil silica hybrid coatings [145]; these exhibited excellent flexibility (Fig. 11). To a mixture of ESO, ELO and functional silane coupling reagent GPTMS, thermally latent catalyst (a benzylsulfonium hexafluoroantimonate derivative) was added. The biodegradability of the ESO–GPTMS nanocomposite was evaluated by BOD measurement in an activated sludge, which reached higher than 50% after two months. Thus, these nanocomposites maybe used as the biodegradable plastics for commodity applications. Another set of

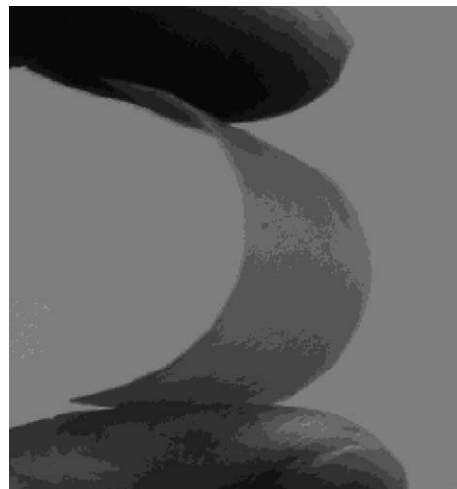


Fig. 11. Photograph of nanocomposite film showing the flexibility. (Reproduced with permission from Hiroshi et al. [145].)

bio-based epoxy nanocomposites has been prepared [146] where CFRP were processed using the bio-based epoxy/clay nanocomposites whereas biodegradation studied were not carried out on these nanocomposites.

2.13. Miscellaneous

A kinetic study on the thermal degradation of phenolic resin/silica hybrid nanocomposites has been reported [147]. Polymer-rich/clay-rich phase separated polymer-layered silicate nanocomposites were prepared through a solution blending of poly(xylylidene tetrahydrothiophenium chloride) with two kinds of layered silicates. Thin films of each phase were obtained by spin-coating, followed by thermal elimination of tetrahydrothiophene and HCl to give a final poly(*p*-phenylenevinylene) (PPV)/layered silicate nanocomposite. At ambient conditions, the PPV films are easily photodegraded due to the oxygen diffused in. Poly(*p*-phenylenevinylene)/layered silicate nanocomposites showed improved environmental stability against photodegradation, under ambient air. Additional optical absorption and photoluminescence measurements demonstrate that the thin films of the clay-rich phase are much less photodegraded than those of polymer–clay rich and PPV.

3. Conclusion and future prospects

In general, nanocomposites of all polymers showed higher thermal stability with dispersion of clay under inert as well as oxygen atmosphere. As far as biodegradability is concerned, there is no confirmation about the mechanisms of bioconsumption in the presence of clay. The degradability under UV light is a serious problem, which may limit the applicability of

these materials. The nanocomposites of most useful commodity polymer (e.g. PP and PE) exhibited less stability than neat polymers. Thus, one may get highly improved material properties by filling the polymer matrix with layered silicates, but the durability in outdoor application is still a challenge and the best way would be to develop nanocomposites by modification in clay rather than functionalisation of thermoplastics to increase the outdoor durability. In preparation of PLA composites thermal degradation has been observed even in the presence of thermal stabilizers which lead the deterioration of properties in the resulting products. Durability of few industrially useful polymeric nanocomposites like polyurethane has not been evaluated in any environment. Nanocomposites especially biodegradable nanocomposites are an emerging new class of materials. These nanocomposites are the wave of the future and considered as the material of next generation. The nanocomposites of starch open a new area in this direction where one may get sufficient material properties by filling it with layered silicate in appropriate way. The moisture sensitivity is still a problem in the starch nanocomposites. It is difficult to draw a conclusion on the mechanisms of degradation (photo, thermal and bio) of nanocomposites on the basis of present literature. Overall there is essential requirement to investigate the durability of these nanocomposites in different environmental conditions to extend the applicability of these hybrid materials.

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