Morphological and Thermal Properties of Photodegradable Biocomposite films

Sreejarani Kesavan Pillai*, Suprakas Sinha Ray, Manfred Scriba, Vincent Ojijo, and Mpitloane Joseph Hato

National Centre for Nano-Structured Materials, Council for Scientific and Industrial Research, P. O. Box 395, Pretoria 0001, South Africa

^{*} Corresponding author E mail: skpillai@csir.co.za; Phone: +27128413759, Fax: +27128412229

Abstract

Biocomposites containing UV absorbing inorganic nanofillers are of great interest in food packaging applications. The biodegradable polylactide (PLA) composite films were prepared by solvent casting method by incorporating 1 wt % of TiO₂ and Ag-TiO₂ nanoparticles to impart the photodegradable properties. The films were exposed to UV irradiation for different time periods and morphology of the composite films before and after UV exposure were investigated. The results showed that homogenous filler distribution was achieved in the case of Ag-TiO₂ nanoparticles. The thermal properties and thermo-mechanical stability of the composite film containing Ag-TiO₂ were found to be much higher than those of neat PLA and PLA/TiO₂ composite films. The scanning electron microscopy and X-ray diffraction studies revealed that the photodegradability of PLA matrix was significantly improved in the presence of Ag-TiO₂ nanoparticles.

Keywords: PLA, TiO₂, and Ag-TiO₂ nanoparticles, photodegradable biocomposite films, thermal and thermo-mechanical properties

1. Introduction

Food packaging is one of the major fields of application for polymeric materials. Because of their non-degradable nature, there is an increasing desire for companies and consumers to reduce, recycle, and reuse plastic packaging materials, which are derived from traditional petrochemical-based polymers or, alternately, substitute them with environmentally friendly polymeric material, which is a more sustainable option. Polylactide (PLA) derived from renewable resources, like corn, sugar beets, wheat, and other starch-rich products, is such a polymer that has shown huge potential to develop biodegradable plastics for textile, medical, and packaging industries. However, neat PLA's inherent

thermal and thermo-mechanical stability are not sufficient for a wide-range of applications.⁴ Another important drawback of PLA is its slower degradation under normal conditions.

Processing polymer composites with inorganic nanoparticles offers a great opportunity to enhance the physical, thermal, and mechanical properties of neat polymers.^{5–7} The effectiveness of fillers with nanometric dimensions strongly depends on its shape, particle size, aggregate size, surface characteristics, and degree of dispersion.^{8, 9} According to classical composite theory, improved interfacial bonding between polymer matrix and filler particles leads to enhance practical properties of the composites.^[10]

PLA composites have been reported using various nanoparticles, including carbon nanotubes, layered silicates or clays, silica, graphite, magnesium oxide, etc. ^{2,7,11–14} Though these composites exhibited enhanced mechanical strength and modulus, very few nanoparticles could efficiently improve the thermal and thermomechanical stability of neat PLA. ^{12, 15} This may be due to the lack of strong interfacial interactions between nanoparticles and PLA matrix.

Although the mechanical, physical, and thermal properties of PLA-based composites are important with respect to their in-house use and storage, ideally, these materials should biodegrade efficiently on disposal. While biodegradation of polymers like PLA takes place at higher rates in compost where moisture and bacteria exist (it does not advance in air), more than three months is needed for the complete decomposition. As an alternative strategy, by incorporating photodegradability to a biodegradable polymer, the overall degradability can be efficiently improved under any conditions. Trainium dioxide (TiO₂) nanoparticles have been investigated in recent years because of the capability to absorb UV light ($\lambda < 388$ nm) and generate oxygen species $^{21, 22}$ that decompose various organic chemicals such as aldehyde, toluene, and polymers such as polyethylene (PE) 23,24 , polypropylene (PP) 25 , poly(vinyl chloride) (PVC) 22 , and polystyrene (PS). It is well known that the photocatalysis reaction of TiO₂ produces active oxygen species such as O₂, HO₂, and HO radicals from H₂O or O₂ by

oxidative or reductive reactions under UV exposures. These active oxygen species will lead to photodegradation reactions by attacking the interfacial polymer chains, forming carbon-centred radicals, and accelerating chain cleavage.²

Research in composites based on TiO₂ and PLA has recently been focused on applications like drug releasing ^{5, 27} degradation of organic pollutants ³, and textiles. ²⁸ A few studies have reported on improved dispersion of TiO₂ nanoparticles in PLA and the resulting PLA/TiO₂ composites' improved photodegradability. However in these investigations, the TiO₂ nanoparticles used were surface modified by using tedious or multi-step procedures to get good interfacial interaction with PLA matrix. ^{2, 29–31} For example, Nakayama et al. ² reported improved photodegradability of PLA composites with TiO₂ nanoparticles modified by propionic acid and n-hexyl amine, independent of the filler content. Luo et al. ²⁹ used functionalized TiO₂ with lactic acid through solution polycondensation reaction for the preparation of PLA/TiO₂ composites. Zhuang and co-workers ²¹ used organically modified TiO₂ to synthesize PLA/TiO₂ composites with improved mechanical and thermal properties by *in situ* polymerization.

In this work, PLA composites were prepared by solvent casting method employing Ag modified TiO₂ without any further surface modification. This is compared to the structural and thermal properties of composites prepared by the same method but using TiO₂ nanoparticles. The effect of different nanofillers to the photodegradation property is also investigated. The powder samples and solvent casted composite films were characterized by X-ray diffraction (XRD), UV-Visible spectroscopy (UV-Vis), scanning electron microscopy (SEM), themogravimetric analysis (TGA), differential scanning calorimetry (DSC), and dynamic mechanical analyzer (DMA).

2. Experimental section

2.1. Materials

PLA with a *D*-lactide content of 1.1–1.7% was obtained from Unitika Co. Ltd, Japan. Prior to use, PLA was dried at 80 °C for 2 h under vacuum. Commercial TiO₂ nanoparticles (P25) with diameter 20–40 nm were supplied by Degussa, Germany. The reagents such as, CHCl₃, NH₄OH, ethylene glycol (EG), and AgNO₃ were purchased from Sigma Aldrich and used as received without further purification.

2.2. Synthesis of Ag-TiO₂ nanoparticles

In a typical synthetic procedure, 1 g of TiO₂ (P25, Degussa) was mixed with 100 ml of 0.01 M AgNO₃ solution and 10 ml ethylene glycol, and magnetically stirred for 24 h at 60 °C. The solid mass was filtered, washed several times with distilled water, and finally dried in the oven at 110 °C overnight.

2.3. Preparation PLA/TiO₂ and PLA/Ag-TiO₂ composite films

PLA composite films with 1 wt % inorganic content (TiO₂ and Ag-TiO₂) were prepared by solvent-casting method. A known weight of PLA was dissolved in 100 ml CHCl₃ by ultrasonication. The inorganic oxide was added to the PLA solutions and magnetically stirred for 2 h at room temperature. The mixture was then poured into Petri dishes, and the solvent was allowed to evaporate overnight. The films were peeled off from the Petri dishes and annealed at 80 °C overnight under vacuum. Neat PLA film was also prepared under the same conditions for comparison.

2.4. Characterization of TiO₂ and Ag-TiO₂ powder samples

The nanoparticle size and shape were analyzed by a JEOL 2100 TEM, operated at 200 kV. To prepare the sample for TEM, the powder was sonicated in methanol for 5 min, followed by depositing the solution on a Cu-grid with holey carbon film. The UV-Vis characteristics of the nanoparticles were recorded by a Perkin-Elmer Lambda 750 UV-Vis spectrometer. The SEM analysis was done using a

JEOL 7500 SEM at an accelerating voltage of 5 kV. Elemental analysis was performed using a NORAN EDS system, which was attached to the JEOL 7500 SEM.

2.5. Characterization of PLA and its TiO₂ or Ag-TiO₂ containing composite films

The following techniques were used to characterize neat PLA and the corresponding composite films before and after UV exposure. Differential scanning calorimetry (DSC) investigations were performed by means of a DSC Q2000 (TA Instruments) in nitrogen atmosphere at a flow rate of 50 ml/min. The samples were sealed in aluminum pans. To study the effect of incorporation of filler on clod crystallization behavior of PLA, all samples were heated from 25 °C to 200 °C at a rate of 5 °C/min, annealed for 5 min at 200 °C to erase previous thermal history, cooled down to 25 °C at 5 °C/min, and then repeated heating scanned immediately to 200 °C at a rate of 5 °C/min. The crystallization peak (T_c) , melting peak (T_m) temperatures, and degree of crystallization (χ_c) were determined from the thermograms. χ_c was calculated according to the relation $\chi_c = [\Delta H_m/\omega \Delta H_f] \times 100$, where ω is the weight fraction of PLA component, $\Delta H_{\rm m}$ is the enthalpy of melting and $\Delta H_{\rm f}$ is the heat of fusion of 100% crystalline PLA (taken as 93 J/g). 32 To study the effect of filler on PLA $T_{\rm g}$, annealed samples (at 80 $^{\circ}$ C for overnight under vacuum) were equilibrated at -25 °C for 30 min and then heated to 200 °C at a rate of 20 °C/min. A field-emission SEM (JEOL 7500 FESEM) was used to characterize the surface morphology of the neat PLA and composite films. The XRD analyses were conducted on a PANalytical XPERT-PRO diffractometer using Ni filtered CuK α radiation ($\lambda = 1.5406$ Å) with a fixed slit at 45 kV (voltage) and 40 mA (current) in the diffraction angle range of 2 to 80 °C. The thermal stability of the neat PLA and two different composite films was investigated by thermogravimetric analyzer using a Q500 TGA instrument in a normal air environment. The samples were heated in platinum crucibles with an air flow of 50 ml/min. The dynamic measurement was conducted from ambient temperature to 900 °C, with a ramp rate of 10 °C/min. The dynamic mechanical analysis of neat PLA and two different composite samples were examined by means of Perkin Elmer DMA 8000 in a single cantilever mode with a pocket material. To measure the thermo-mechanical stability of neat PLA, before and after composites formation, the temperature sweep experiments were conducted at a constant strain amplitude of 0.02% (calculated after series of experiments) and frequency of 6.28 rad.s⁻¹ (1Hz). The heating rate was 2 °C/min over the range of -25 to 175 °C.

2.6. Degradation study under UV light

Annealed neat PLA and composite films were cut into rectangles and mounted on glass plates. The samples were then exposed to UV monochromatic light (λ =365 nm) in a UV chamber for two irradiation intervals of 8 and 16 h (sample notation, e.g., PLA' and PLA'') at room temperature. The distance between the UV lamp and the sample was 15 cm at an intensity of 950 μ W cm⁻².

3. Results and discussion

3.1. Morphology and structure of TiO_2 and $Ag-TiO_2$ nanoparticles

Parts (a) and (b) of Figure 1 show the TEM images of TiO₂ and Ag-TiO₂, respectively. The TiO₂ has a grain distribution of 20–50 nm and typically the exposed surfaces are smoother (refer to Figure 1(a)). The TEM image of Ag-TiO₂ presented in Figure 1(b) shows uniform distribution of Ag nanoparticles with a mean diameter less than 5 nm, on the surface of TiO₂ particles. One could clearly notice the change in the surface morphology, i.e., increased surface roughness of the TiO₂ nanoparticles due to the deposition of Ag.

The FESEM image of Ag-TiO₂ sample and its EDS spectrum is shown in Figure 1(c). TiO₂ nanoparticles with particle sizes in the 20–50 nm can be seen in the SEM micrograph. Though the presence of Ag nanoparticles on the TiO₂ surface is not clearly visible from the micrograph, the EDS spectrum (refer to Figure 1(d)) shows the characteristic signals of Ti, O, and Ag confirming the successful incorporation of Ag into TiO₂ and the high purity of the synthesized material. The average concentration of Ag on TiO₂ obtained from multi-spot analysis is close to 3.95 wt % (1.3 at %).

The UV-Vis spectra of TiO₂ and Ag-TiO₂ nanoparticles are shown in Figure 2. A broad band absorption ranging from 250–350 nm is observed for both samples. However, it is noteworthy that Ag-TiO₂ sample shows an absorption band, upward shifted (blue shifted) relative to that of TiO₂ nanoparticles. The blue shift is ascribed to a phenomenon known as quantum confinement effect, whereas in the case of nanoparticles with much smaller size; the optical edge tends to shift to higher energy. ^{33, 34} In the case of Ag-TiO₂ sample, the blue shift is due to the presence of additional, very small sized Ag nanoparticles on the TiO₂ surface.

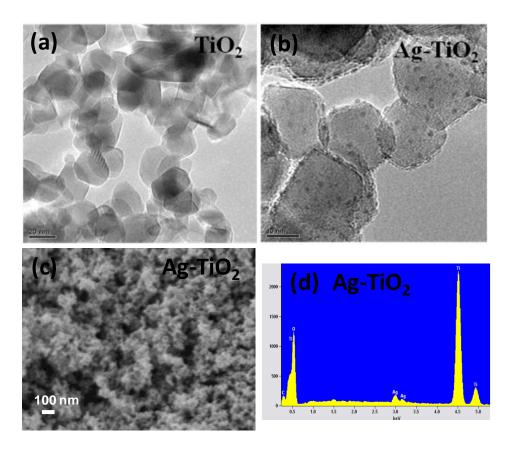


Figure 1 Bright field transmission electron microscopic image of (a) TiO₂ and Ag-TiO₂ nanocparticles. (b) Field-emission scanning electron microscopic image of Ag-TiO₂ nanoparticles and (c) corresponding energy-dispersive X-ray spectrum.

The XRD patterns in Figure 3 show tetragonal anatase as the predominant crystalline phase of TiO₂ in both TiO₂ and Ag-TiO₂ samples (reference code: 01-075-1537). The Ag-TiO₂ sample shows less

intense additional peaks at $2\theta = 44.4$ and 77.2 °C, confirming the presence of a cubic phase of Ag nanoparticles (reference code: 00-003-09210).

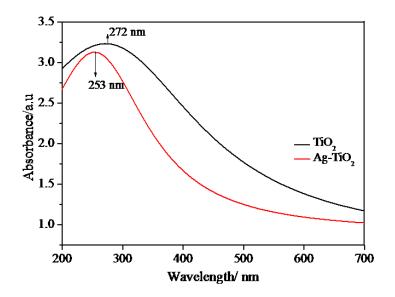


Figure 2 UV-Vis absorption spectra of TiO₂ and Ag-TiO₂ nanoparticles

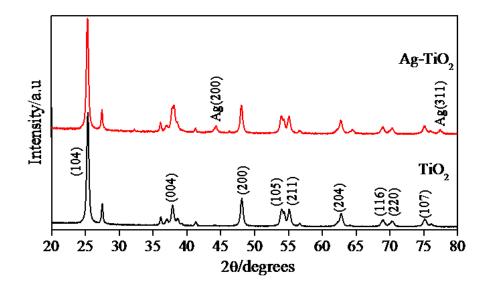


Figure 3 X-ray diffraction patterns of TiO₂ and Ag-TiO₂ nanoparticles

3.2. Fractured surface morphology of composite films

The TiO₂ and Ag-TiO₂ nanoparticle distribution and the presence of their aggregates in PLA matrix were studied with FESEM. Parts (a) and (b) of Figure 4, respectively, show the fractured-surface morphology of PLA/TiO₂ and PLA/Ag-TiO₂ composite films. PLA loaded with 1 wt % Ag-TiO₂ shows

a reasonably good degree of dispersion with fewer tendencies of nanoparticles for aggregation when compared to PLA/TiO₂ composite containing the same amount of TiO₂ loading. The surface roughness of the polymer observed in PLA/TiO₂ is higher with respect to PLA/Ag-TiO₂ indicating a higher degree of nanoparticle aggregation in the case of PLA/TiO₂ composite film. The SEM micrograph of PLA/Ag-TiO₂ also shows well-embedded Ag-TiO₂ nanoparticles with no pull-outs during fracture, illustrating strong binding between the Ag-TiO₂ and the PLA matrix. This may be due to the very rough surface of Ag-TiO₂ nanoparticles (refer to the TEM images in Figure 1), which leads to the strong adsorption of PLA chains on Ag-TiO₂ surface. We will confirm this as we progress.

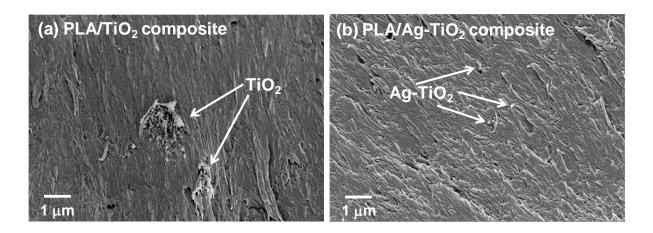


Figure 4 Field-emission scanning electron microscopy fractured-surface image of (a) PLA/TiO₂ and (b) PLA/Ag-TiO₂ composite films.

3.3. Thermal stability

The TGA scans for neat PLA and two different composite samples (PLA/TiO₂ and PLA/Ag-TiO₂) are presented in Figure 5. Table 1 shows the onset decomposition temperature (at 5 % weight loss), the temperature at 10% weight loss, and char yield (at 600 °C) for the samples. The initial decomposition temperature of neat PLA is 263 °C (at 5 % weight loss), which is significantly shifted to a higher value for PLA/Ag-TiO₂ composite (290.1 °C), whereas the value is decreased in the case of PLA/TiO₂ composite film (261.5 °C) as compared to neat PLA film. This may be due to the poor adhesion of TiO₂ smooth surfaces to the PLA matrix.² Furthermore, the higher thermal stability of PLA/Ag-TiO₂ composite could be attributed to a good dispersion of Ag-TiO₂ nanoparticles in PLA matrix.

According to the TEM images (refer to Figure 1), Ag-TiO₂ nanoparticles have rough surfaces, which lead to better adsorption of PLA chains on Ag-TiO₂. Another reason may be the presence of higher thermally stable Ag nanoparticles in Ag-TiO₂, which contribute to the enhancement of the overall thermal stability of PLA/Ag-TiO₂ composite. The residue obtained at 600 °C for neat PLA is 0.03% while those of composites are in the range 0.8-0.9%.

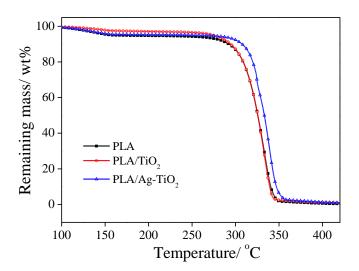


Figure 5 Thermogravimetric scans of neat PLA and two different composite films under air.

Table 1. Data calculated from TGA analysis.

Films	T _d onset/ oC	T _d ^{10%} /°C	Residue at 600 °C/%
PLA	263.7	290.7	0.03
PLA/TiO ₂	261.5	293.8	0.92
PLA/Ag-TiO ₂	290.1	306.1	0.84

3.4. Thermal properties

Figure 6(a) shows the DSC thermograms of annealed neat PLA and composite films. Figure 6(b) shows the DSC thermograms of neat PLA and the composites after erasing the previous thermal history, and the parameters determined from these DSC scans are tabulated in Table 2. The following features are observed, mainly:

(i) The $T_{\rm g}$ for all samples is seen clearly (refer to Figure 6(a)). Such an observation indicates all samples are constraint free after annealing at 80 °C overnight. The $T_{\rm g}$ of neat PLA (54.7 °C) is slightly increased in the case of the PLA/TiO₂ (55.7 °C) composite. This may be due to the unfavorable interaction between PLA matrix and TiO₂ particles, while the $T_{\rm g}$ of neat PLA is significantly improved in the case of PLA/Ag-TiO₂ composite film. This is quite unusual in the case of PLA-based composite. We believe this is due to the strong adsorption of PLA macromolecules on the rough Ag-TiO₂ surface because FTIR analysis (refer to Figure 7) did not show the presence of any chemical interaction between the PLA matrix and Ag-TiO₂ nanoparticles.

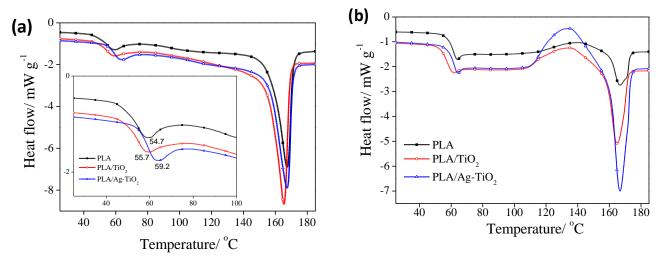


Figure 6 DSC thermograms of neat PLA and the composite films: (a) annealed samples, first runs and (b) from second runs.

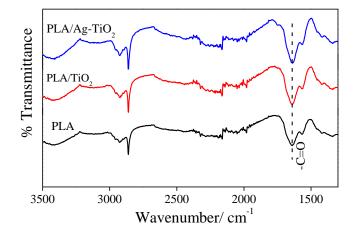


Figure 7. Fourier-transform infrared spectra of neat PLA and composite films.

(ii) A sharp cold-crystallization peak appears for all samples. Such a result indicates that, for all samples, the cold crystallization process of PLA matrix takes place from a single homogeneous phase. However, it is interesting to note that the cold crystallization peak temperature of neat PLA moves towards much lower temperatures in the case of composites, and it is significant in the case of PLA/Ag-TiO₂ composite. This indicates an efficient nucleating role of the Ag-TiO₂ nanoparticles for PLA crystallization. We believe this is due to the homogeneous dispersion of Ag-TiO₂ nanoparticles in the PLA matrix, which consequently act as nucleators of the PLA chains to fold and join the crystallization growth front efficiently. This is supported by the higher overall crystallinity of PLA/Ag-TiO₂ composite (refer to Table 2).

Table 2 Thermal properties of neat PLA and two different composite films

Films	T _g /°C	T _c /°C	T _m /°C	$\Delta H_{\rm c}/~{ m J~g^{-1}}$	$\Delta H_{\rm m}/{\rm J g}^{-1}$	χ _c / %
PLA	54.7	140.1	166.6	6.5	6.8	7.3
PLA/TiO ₂	55.7	135.3	164.6	14	15.02	16.5
PLA/Ag-TiO ₂	59.2	134.1	164.3	24	25.1	27.9

(iii) The melting peak temperature (corresponding to the main peak) of the composites shifts to the lower temperature region than that of neat PLA, and this effect is more prominent in the case of the PLA/Ag-TiO₂ composite (refer to Figure 6(b)). Such results indicate the formation of much smaller crystallites in the case of composites than neat PLA. The appearance of double melting peaks in the case of composites suggests the presence of two different types of thermally stable PLA crystallites; however, there is a significant difference in population.

3.5. Thermo-mechanical stability

The temperature dependence of tan δ of neat PLA and composites are presented in Figure 8. The temperature of loss tan δ of neat PLA film is generally considered as matrix $T_{\rm g}$ (66.3 °C), which is slightly affected by incorporation of TiO₂ nanoparticles in the case of PLA/TiO₂ composite. However,

this improvement is significant in the case of PLA/Ag-TiO₂ composite film. Such a unique observation in the case of Ag-TiO₂ nanoparticle-containing composite of PLA supports strong adsorption of PLA chains on rough Ag-TiO₂ surfaces. This lead to the immobilization of PLA chains and, hence, enhanced thermo-mechanical properties. This is a very important improvement in the case of PLA composite.

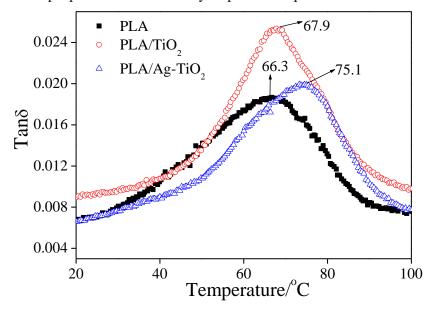


Figure 8 Temperature dependence of tan δ of neat PLA and composite films.

3.6. Crystalline structure

The crystalline structure of neat PLA before and after composite preparation was studied using XRD. The XRD patterns of annealed neat PLA and the composites are shown in Figure 9. It can be seen that the neat PLA film exhibits a very strong peak at $2\theta = 16.8^{\circ}$ due to reflection from (200) and/110 planes, and another less intense peak at $2\theta = 19.5^{\circ}$ coming from the (203) plane. These peaks are assigned to the reflection of α -phase crystallite of PLA, which is orthorhombic with chains in a -10/3 helical conformation.³⁵ In the case of PLA/TiO₂ composite film, these characteristic peaks of the PLA matrix appear almost at the same positions, while both peaks are slightly up-shifted in the case of PLA/Ag-TiO₂ composite film. Such an observation indicates that PLA matrix crystallized in a defect-ridden form in the case of PLA/Ag-TiO₂ composite. This type of growth of PLA crystallites may be due to the homogeneous dispersion of Ag-TiO₂ nanoparticles in PLA/Ag-TiO₂ composite film.

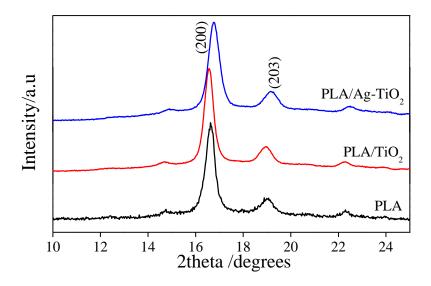


Figure 9 X-ray diffraction patterns of annealed neat PLA and composite films.

3.7. Photodegradation

To study the photodegradation, neat PLA and its composite films containing TiO_2 and $Ag-TiO_2$ nanoparticles were exposed to UV light (wave length, $\lambda = 365$ nm) for two different time intervals of 8 and 16 h, thereafter the films surface morphology and crystalline structure of PLA were respectively analyzed using SEM and XRD. From the SEM images shown in Figure 10, it is clear that the degradation of neat PLA film gradually increases with increased UV exposure time as indicated by the number of small cracks on the PLA surface. In the case of PLA/TiO₂ composite film, the degradation rate is initially higher but decreases with higher exposure time. Since TiO_2 nanoparticles have the ability to absorb the UV radiation, it seems that they suppress the photodegradation and protect the remaining PLA surface when TiO_2 nanoparticles were directly exposed to the UV light after degradation of matrix. Nakayama reported similar observations on PLA films containing a higher amount (~10 wt %) of TiO_2 .²

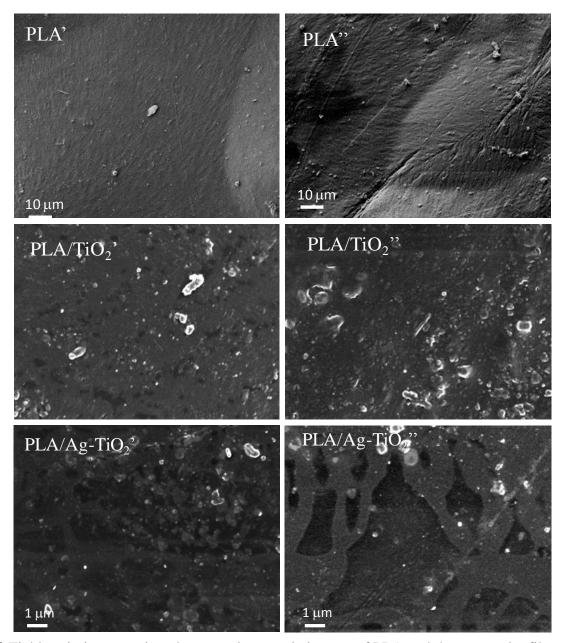


Figure 10 Field-emission scanning electron microscopic images of PLA and the composite films after UV exposure for 8 (') and 16 h (").

On the other hand, the PLA composite film filled with Ag-TiO₂ nanoparticles shows the highest degradation rate among all the films, which significantly improves after 16 h of UV exposure. The surface of the composite is obviously degraded to a greater extent, with a noticeable increase in the size of the cavities (refer to Figure 10).

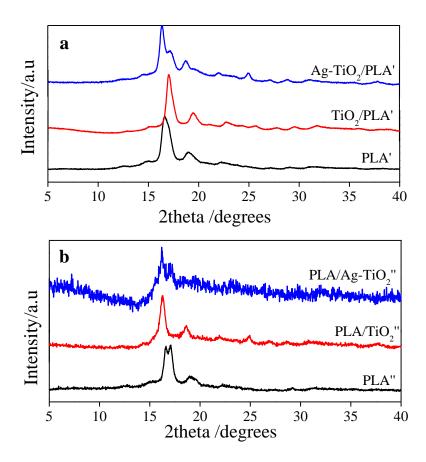
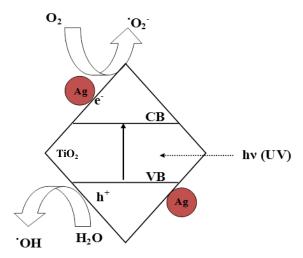


Figure 11 X-ray diffraction pattern of neat PLA and the composite films after UV exposure: (a) 8 h and (b) 16 h

The XRD patterns of neat PLA and composite films after UV exposure, at two different times, are given in Figure 11. The increase degradation rate of PLA matrix with exposure time is reflected by the splitting of the main crystalline peak of PLA matrix after 16 h of UV irradiation. The efficient degradation rate in PLA/Ag-TiO₂ composite, when compared to PLA/TiO₂ film, is clearly seen from the significant reduction in the peak intensity of PLA as a result of efficient photodegradation. The split XRD peak is observed from 8 h of UV exposure in this case. This result also indicates that the Ag content on the TiO₂ surface is within the range of maximum photonic efficiency (1.5 at %-optimum Ag loading).³⁶



Scheme 1 Pathway of charge transfer in Ag-TiO₂ under UV irradiation (VB- valence band, CB-conduction band)

It is well reported that noble metals like Pt ³⁷, Au ³⁸, or Ag ³⁹ deposited TiO₂ have high Schottky barriers and thus act as electron traps, facilitating electron-hole separation and promote an interfacial electron transfer process. ^{40,41} In this case, Ag nanoparticles accept the electrons formed on TiO₂ surface under UV radiation thereby reducing the electron-hole pair re-combination, and transfer them to oxygen forming active oxygen species (refer Scheme 1). ⁴² The active oxygen species initiate the degradation by attacking the interfacial PLA chains, and this process is extended to the matrix through diffusion of reactive oxygen species.² This phenomenon describes the more efficient and faster degradation of PLA/Ag-TiO₂ nanocomposite film in comparison to PLA/TiO₂ under UV irradiation.

4. Conclusions

The TiO₂ and Ag-TiO₂ nanoparticles, without any further surface modification, were successfully incorporated as fillers in biodegradable PLA matrix by solvent casting technique. The overall thermal stability of the PLA composite film containing Ag-TiO₂ was found to be much higher than that of neat PLA and PLA/TiO₂ composite films. The overall degree of crystallinity and thermomechanical stability of PLA matrix was significantly increased for PLA/Ag-TiO₂. The photodegradation rate of PLA was also drastically enhanced by incorporating Ag-TiO₂ nanofillers. All these results are attributed to the

homogenous dispersion of Ag-TiO₂ nanoparticles in PLA matrix. The Ag nanoparticles on TiO₂ surface play an important role in increasing the surface roughness of TiO₂ nanoparticles for better interaction with the PLA matrix as well as for the overall UV degradation ability of the resultant composite. In our ongoing research, we are trying to fine tune the size of Ag-TiO₂ nanoparticles in such a way that they can absorb light in the visible region. We are also diligently working to understand the interfacial properties of Ag-TiO₂ nanoparticles and PLA matrix.

Acknowledgements

The authors thank the Department of Science and Technology (DST) and the Council for Scientific and Industrial Research (CSIR), South Africa, for the financial support.

References

- [1] Piringer, O.; Baner, A. Plastic Packaging, 2nd Edition, Wiley-VCH Velag GmbH & Co. KGaA, 2008, p.2
- [2] (a) Ojijo, V.; Sinha Ray, S.; Sadiku, R. ACS Appl. Mater. Interfces 2012, 4,2395.
 - (b) Nakayama, N.; Hayashi, T. *Polym. Degrad. Stab.* **2007**, 92, 1255.
- [3] Zhu, Y.; Buonocor, G.G.; Lavorgna, M.; Ambrosio, L. Polym. Comp. 2011, 32,435.
- [4] Sinha Ray, S.; Bousmina, M.; Prog. Mater. Sci. 2005, 50, 962.
- [5] Chen, C.; Lv, G.; Pan, C.; Song, M.; Wu, C.; Guo, D.; Wang, X.; Chen, B.; Gu, Z. *Biomed. Mater.* **2007**,2, L1.
- [6] Paul, D.R.; Robeson, L. M. Polymer 2008, 49,3187.
- [7] Sinha Ray, S.; Maiti, P.; Okamoto, M.; Yamada, K.; Ueda, K. Macromolecules 2002, 35, 3104.
- [8] Curtin, W. A.; Sheldon, W. B. *Mater. Today* 2004,7,44.
- [9] Chan, C.M.; Wu, J.; Li, J.X.; Cheung, Y. K. Polymer 2002, 43, 2981.
- [10] Ciprai, D.; Jacob, K.; Tannenbaum, R. Macromolecules 2006, 39,6565.
- [11] Nam, J.Y.; Sinha Ray, S.; Okamoto. M. *Macromolecules* **2003**, 36, 7126.

- [12] Wu, C. S.; Liao, H. T. *Polymer* **2007**, 48, 4449.
- [13] Song, W.; Zheng, Z.; Tang, W.; Wang. X. Polymer 2007, 48, 3658.
- [14] Yan, S.; Yin, J.; Yang, Y.; Dai, Z.; Ma, J.; Chen, X. Polymer 2007, 48, 1688.
- [15] Tsuji, H.; Takai, H.; Saha, S.K. Polymer **2006**, 47, 3826.
- [16] Shogren, R. L.; Doane, W.M.; Garlotta, D.; Lawton, J. W.; Willett, J. L. *Polym. Degrad. Stab.* **2003**, 79, 405.
- [17] Ikada, E. J. J. Photopolym. Sci. Technol. 1997, 10,265.
- [18] Ikada, E.J. J. Photopolym. Sci. Technol. 1998, 11, 23.
- [19] Copinet, A.; Bertrand, C. S.; Govindin, V.; Coma, Couturier, Y. Chemosphere 2004, 55,763.
- [20] Copinet, A.; Bertrand, C.; Longieras, A.; Coma, V.; Couturier, Y. J. Polym. Environ. 2003, 11, 169.
- [21] Zhuang, W.; Liu, J.; Zhang, J. H.; Hu, B.X.; Shen, J. J. Polym. Compos. 2009, 30, 1074.
- [22] Zan, L.; Wang, S.; Fa, W.; Hu, Y.; Tian, L.; Deng, K. Polymer 2006, 47,8155.
- [23] Ohtani, B.; Adzuma, S.; Nishimoto, S. I.; Kagiya, T. Polym. Degrad. Stab. 1992, 35, 53.
- [24] Zan, L.; Fa, W.; Wang, S. Environ. Sci. Technol. 2006, 40, 1681.
- [25] Ohtani, B.; Adzuma, S.; Miyadzu, H.; Nishimoto, S. I.; Kagiya, T. *Polym. Degrad. Stab.* **1989**, 23, 271.
- [26] Kim, S.H.; Kwak, S.Y.; Suzuki, T. *Polymer* **2006**, 47, 3005.
- [27] Song, M.; Pan, C.; Chen, C.; Li, J.; Wang, X.; Gu, Z. Appl. Surf. Sci. 2008, 255, 610.
- [28] Carneiro, J.O.; Teixeira, V.; Nascimento, J. H. O.; Neves, J.; Tavares, P. B. J. Nanosci. Nanotechnol. 2011, 11, 1-8.
- [29] Luo, Y.B.; Li, W.D.; Wang, X. L.; Xu, D. Y.; Wang, Y. Z. Acta Material. 2009, 57, 3182.
- [30] Luo, Y.B.; Wang, X.L.; Xu, D.Y.; Wang, Y.Z. Appl. Surf. Sci. 2009, 255, 6795.
- [31] Nakayama, N.; Hayashi, T. Colloids Surfaces A: Physicochem. Eng. Asp. 2008, 317, 543.

- [32] Fischer, E. W.; Sterzel, H.J.; Wegner, G. Kolloid-Zeitschrift & Zeitschrift for Polymere 1973, 251,980.
- [33] Mao, Y.; Wong, S. S. J. Am. Chem. Soc. 2006, 128, 8217.
- [34] Cesano, S. B. F.; Uddin, M. J.; Agostini, G.; Scarano, D.; Zecchina, A. J. Phys. Chem. C 2010, 114, 169.
- [35] Schmidt, S. C.; Hillmyer, M. A. J. Polym. Sci. Part B: Polym. Phys. 2001, 39, 300.
- [36] Herrmann, J.M.; Disdier, J.; Pichat, P.; Malato, S.; Blanco, J. Appl. Catal. B: Environ. 1998, 17,15.
- [37] Li, Y.; Chen, C.; Li, J.; Sun, X. S. Polymer **2011**, 52, 2367.
- [38] Buzarovska, A.; Grozdanov, A. J. Appl. Polym. Sci. 2011, 123, 2187.
- [39] Brizzolara, D.; Cantow, H.J.; Diederichs, K.; Keller, E.; Domb, A. J. *Macromolecules* **1996**, 29, 191.
- [40] Sclafani, A.; Palmisano, L.; Marcil, G.; Venezia, A. M. Solar Energy Mater. Solar Cells 1998, 51, 203.
- [41] Wang, C. Y.; Liu, C. Y.; Zheng, X. Chen, J.; Shen, T. Colloids Surfaces A: Physicochem. Eng. Asp. 1998, 131, 271.
- [42] Chen, K. W.; Ku, Y.; Kuo, Y. L. Chem. Eng. Technol. 2007, 30, 1242.

Graphical Abstract

Interesting UV degradation properties of Polylactic acid (PLA) films containing TiO_2 and Ag - TiO_2 nanofillers are reported. The Ag- TiO_2 offers better dispersion in PLA matrix due to surface roughness and thereby improves the thermal and degradation properties of the composite film.

