

UV IRRADIATION EFFECT ON THE PROPERTIES OF POLYPROPYLENE / POLYCAPROLACTONE BLENDS CONTAINING NANO TiO₂ PARTICLES

GOVORČIN BAJSIĆ Emi^{1*}, OCELIĆ BULATOVIĆ Vesna¹, FILIPAN Veljko¹,
SUTLOVIĆ Igor¹, JEMRIĆ Tomislav²

¹*University of Zagreb, Faculty of Chemical Engineering and Technology, Zagreb, Croatia, EU*

²*University of Zagreb, Faculty of Agriculture, Zagreb, Croatia, EU*

Abstract

Environmentally friendly polymers can be produced by modification of non-biodegradable synthetic polymers with a biodegradable polymer. Polypropylene (PP) is a thermoplastic polymer difficult to be decomposed by microorganisms in environment. On the other side, polycaprolactone (PCL) is nontoxic, biodegradable polymer material which can be blended with various synthetic polymers over a wide composition range. The aim of this work is therefore to investigate the possibilities of improvement the properties of PP as well as its biodegradability by blending with biodegradable PCL. The main problem in preparation of PP/PCL polymer blends is compatibility between polymers. In this work there are presented the thermal properties and compatibility of PP and PCL polymer blends reinforced with nano sized titan dioxide (nTiO₂) particles as well as effect of nTiO₂ reinforcement before and after UV irradiation. The neat polymers, PP/PCL and PP/PCL/nTiO₂ polymer blends were prepared by melt compounding within a twin screw extruder, while the granules of the blends were compression moulded in a hydraulic press. The thermal properties of the neat polymers, PP/PCL and PP/PCL/nTiO₂ blends are measured using the differential scanning calorimetry, dynamic mechanical analysis and thermogravimetry techniques. The obtained results show that the particles of nTiO₂ as filler in PP/PCL blends have the photocatalytic effect and improve the photocatalytic degradation during UV irradiation. Furthermore, photodegradation process might occur through chain scission reactions, crosslinking and consequently photocatalytic degradation of these polymers.

Keywords: Polypropylene, polycaprolactone, nTiO₂, thermal stability, polymers blends, thermal properties

1. INTRODUCTION

Plastics play a major role in environmental pollution and the dumping of plastic waste into the environment has caused serious problems to flora and fauna. Unlike natural polymers, most synthetic polymers cannot be decomposed by microorganisms, hence the landfill approach becomes inefficient, and other plastics waste management should be found [1]. Modification of non-biodegradable synthetic polymers with a biodegradable polymer producing environmentally friendly polymers is one of the alternative methods to solve this problem. Poly(ϵ -caprolactone) (PCL) is more and more popular due its excellent biodegradability, biocompatibility and bioresorbability [2]. PCL is semicrystalline biodegradable and noncytotoxic polymer with outstanding permeability to thermal properties currently used as biomaterial [3]. Polypropylene (PP) has a high crystallinity which imparts properties such as high tensile strength, stiffness and hardness, but also brittleness and high melting point. This polymer resists humidity and chemicals but it is easily oxidized due to the presence of tertiary carbon atoms in the backbone chain. When polymer is used in outdoor applications, the environment negatively influences the service-life. Photodegradation is degradation of a photodegradable molecule caused by the absorption of photons. Photodegradation causes photooxidative degradation which results in breaking of the polymer chains or crosslinking, produces radicals and reduces the molecular weight, causing deterioration of mechanical properties and leading to useless materials, after an unpredictable time. Among various types of photocatalysts, TiO₂ (commonly known as Titania) is extensively used for degradation of organic pollutants. Titania is a promising photocatalyst due to its inexpensiveness, good photo stability, non-toxicity, and high-reactivity [4]. Titania nanoparticles absorb in the UV region, and hence when blended with

the polymer they absorb UV light effectively. Upon UV irradiation, TiO₂ nanoparticles generate electrons and holes which promote the formation of free radicals. These radicals can react with polymer materials and result in their oxidation and decomposition. Our motivation for this work is therefore to investigate the possibilities of improvement the properties of PP as well as its biodegradability by blending it with biodegradable PCL and reinforced with nano sized titan dioxide (nTiO₂) particles where PP is one of the most studied polymers, PCL is one of the most studied biopolymers and TiO₂ has been widely used for photodegradation of polymers due to its photocatalytic behaviour. In this work, we present the results obtained from the photodegradation experiments of PP/PCL and PP/PCL/nTiO₂ blends. The effect of UV radiation and photocatalytic degradation on the thermal properties of blends was studied. Photodegradation experiments were carried out under simulated sunlight irradiation, to approach real situations of a material disposed in landfills.

2. EXPERIMENTAL

2.1. Materials

Isotactic polypropylene (iPP) (Moplen 500N) was supplied by Basel Polyolefines, Germany, MFI 12 g/10min, $\rho=0.9$ g cm⁻³ at 230 °C. The PCL (Polycaprolactone 440744-500G) average molecular mass M_n of 70,000-90,000 g/mol by GPC, $M_w/M_n < 2$, density 1.145 g/mL at 25° C was supplied by Sigma-Aldrich, Germany. TiO₂ nano powder (denoted as nTiO₂, particles 21 nm, commercial grade Aerioxide P25) was supplied by Sigma-Aldrich, Germany.

2.2. Sample preparation

The compounding of PP and PCL with nTiO₂ content of 5 wt. % was performed with a Rondol 21mm LAB TWIN twin-screw extruder. The temperatures of the five zones were 170 °C, 180 °C, 180 °C, 200 °C and 200 °C from the feeding zone to the die and the rotation speed of 60 min⁻¹ was used. The samples used for the measurements were prepared by pressing the extruded granules in a hydraulic press Dake Model 44-226 at 190°C.

2.3. UV irradiation

The photodegradation of PCL samples was investigated in air at a temperature of 40 °C, using a low-pressure mercury lamp unit (ultraviolet chamber Suntest) which emits radiation at $\lambda= 290$ nm. Irradiation time was 30 days.

2.4. Experimental techniques

2.4.1. Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis (DMA) experiments were performed using a DMA 983 Analyzer (TA). The mean dimensions of specimens were (20.00 x 12.00 x 3.00 mm). The storage E' and loss modulus E'' were recorded at 1Hz and at the heating rate of 3 °C min in a wide temperature range (-100 °C to 150°C). DMA testing was carried out on three samples per material. The loss and storage moduli (E'', E') were recorded as a function of temperature, and the glass transition temperature (T_g) was taken to be the maximum of the loss moduli versus temperature curve.

2.4.2. Differential scanning calorimetry (DSC)

Thermal transitions (melting T_m , crystallization T_c temperatures as well as degree of crystallinity (χ_c) of the blends before and after irradiation were measured using a Mettler Toledo DSC 822^e calorimeter according to the ASTM D-3418-82 standard under N₂ as purge gas. The samples were measured over the temperature

range -100 °C to 190 °C during heating and cooling at a heating rate of 10°C/min. The degree of crystallinities (χ_c) of the samples was evaluated according to the following equation:

$$\chi_c = \Delta H_m / \Delta H_m^0 \times (1 - \% w_{TiO_2} / 100) \times 100 \quad (1)$$

where ΔH_m is the experimental melting enthalpy obtained by DSC measurement and ΔH_m^0 is the melting enthalpy of the completely crystalline PP (165 J/g [5]) and PCL (142 J/g [6]).

2.4.3. Thermogravimetric analysis (TGA)

Thermal stability of the blends before and after UV irradiation was determined with a TA Instruments Q500 system analyser. About 10.0±0.5 mg of each sample was placed in a platinum pan and heated from 25 to 600 °C at a heating rate of 10°C min⁻¹ under nitrogen atmosphere (60 ml/min).

3. RESULTS AND DISCUSSION

3.1. PP/PCL blends dynamic mechanical behaviour-before and after UV irradiation

DMA allows determining the viscoelastic properties and provides information on the glass transition temperature T_g (above which significant chain motion takes place) of the all PP/PCL blends. The temperature dependence of loss modulus (E'') for unirradiated and irradiated PP/PCL/nTiO₂ blends are shown in **Figure 1** and **2**, respectively. Figures show two distinct T_g 's at -54.1 °C [7] and 19, 7°C [8] which are related to PCL and PP, respectively. α_c relaxation as shoulder on PP maximum has been attributed to motion of an amorphous phase in crystalline phase of PP. The T_g values obtained from the curves in the DMA measurements for all blends are shown in **Table 1**. The results given in **Table 1** indicate that the T_g 's of the PP and PCL shift towards to each other with increase in PCL content. This behaviour indicated on partial miscibility at the polymer-polymer interfaces. In the presence of TiO₂ nanoparticles the T_g of PP and PCL in the PP/PCL/nTiO₂ blends were respectively at lower and higher temperatures than those of the neat polymers, which mean that nanoparticle addition reduced the chain mobilities of these polymers and also that better miscibility had been achieved. After UV irradiation, the T_g of PP decreased and PCL increased in PP/PCL/nTiO₂ blends compared to unirradiated blends. This behaviour can be attributed to oxidative degradation which further leads to the chain scission during UV irradiation which is enhanced with TiO₂ nanoparticles. The results indicate that UV degradation is further supported by the photocatalytic activity of the nTiO₂ particles which enhances the degradation process because nTiO₂ particles acts as a photocatalyst, i.e. it accelerates the chemical reaction of degradation.

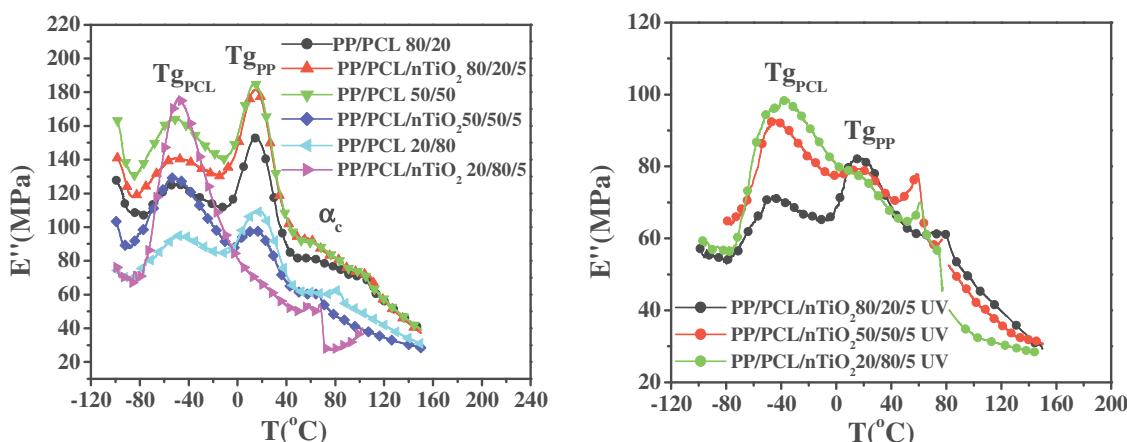


Figure 1 Loss modulus (E'') of the of the PP/PCL blends without and with TiO₂ before and after UV irradiation

As it can be noted from **Table 1**, the storage modulus for the PP/PCL/nTiO₂ blends decreased after UV irradiation due to the photocatalytic activity of the TiO₂ nanoparticles which accelerates the process of blends degradation.

3.2. PP/PCL blends thermal behaviour-before and after UV irradiation

DSC measurements were used to determine the change of the melting temperatures (T_m) and crystallinity (χ_c) of PP/PCL/nTiO₂ blends with UV irradiation. **Figure 2** shows the DSC second heating and cooling curves of PP/PCL blends with 20 and 80 wt % of PCL in PP before and after UV irradiation. The melting temperatures of crystalline phase of PP and PCL were determined to be 165.1 °C and 57.4 °C, respectively (**Table 1**). However, the DSC curves of polymer blends show two peaks associated with the melting temperatures of their component polymers. For PP/PCL blends, the T_m did not change very much by the addition of the TiO₂ nanoparticles as given in **Table 1**. On the other hand, the degree of crystallinity of PP decreased due to the retarding effect of the TiO₂ on PP crystals and physical hindrance of TiO₂ particles to the motion of polymer molecular chains.

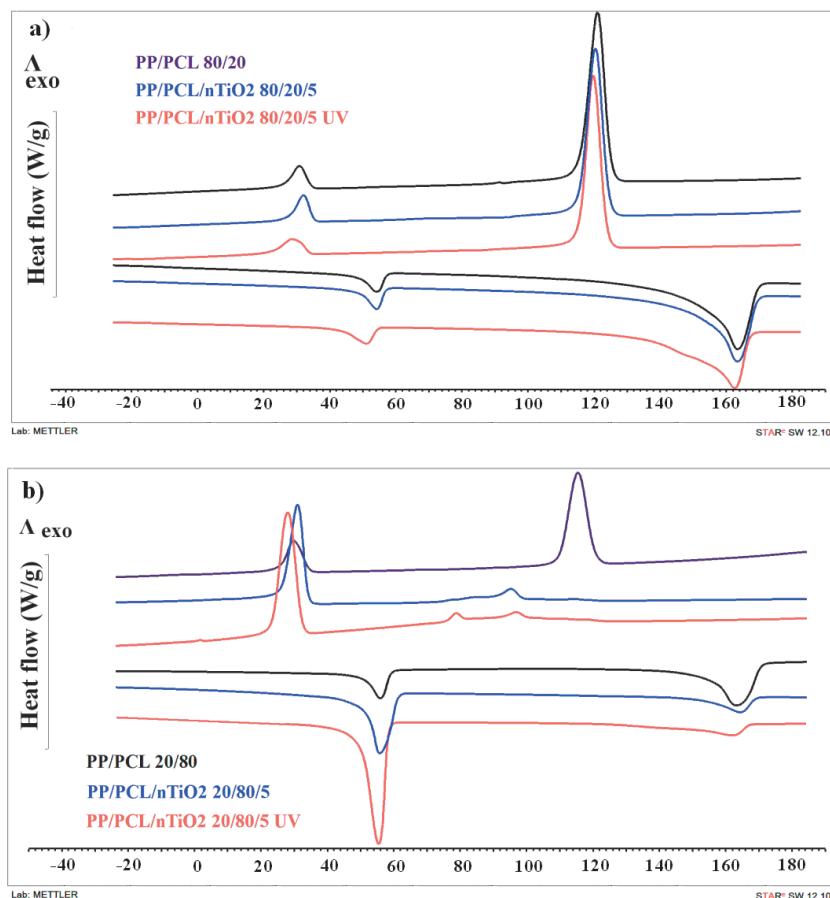


Figure 2 DSC heating and cooling curves of a) PP/PCL 80/20 and b) PP/PCL 20/80 blends without and with TiO₂ before and after UV irradiation respectively

However, increase in degree of crystallinity was seen for PCL. This increment was probably due to the nucleating agent effect of the TiO₂. As shown in **Table 1**, results revealed that crystallinity degree of PP and PCL was increased after UV irradiation. According to the results, due to the photocatalytic nature of TiO₂, TiO₂ absorbs UV light photons and promotes the formation of radicals HO[•], O₂^{•-}, HO₂ resulted in the chain scission and chain branching. Increasing the degree of crosslinking increased mobility of polymer chains and increased the crystallinity degree. Also, these radicals are responsible for the TiO₂ photocatalytic activity.

3.3 PP/PCL blends thermal stability-before and after UV irradiation

Thermogravimetric analysis (TG) provides quantitative information about the thermal decomposition of the polymeric materials, from which the thermal stability can be evaluated. **Figure 3** shows the TG curves for unirradiated and irradiated PP/PCL blends. The initial degradation temperature (T_{onset}) of the neat PP and PCL and unirradiated and irradiated PP/PCL blends taken from the TG thermograms are summarized in **Table 1**.

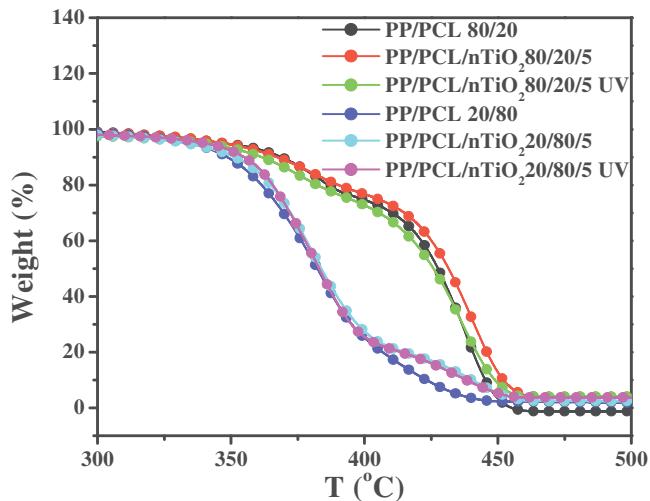


Figure 3 TG curves of the PP/PCL PP/PCL 80/20 and PP/PCL 20/80 blends without and with TiO₂ before and after UV irradiation

Table 1 Thermal properties of PP/PCL blends before and after UV irradiation

Sample	T_g (°C) from DMA		E'25°C (GPa)	T_m (°C)		χ_c (%)		T_{ons} (°C)	
	PP	PCL		PP	PCL	PP	PCL	PP	PCL
PP	-	-54.1	2.3710	165.1	-	59.7	-	420.2	-
PCL	19.7	-	0.6033	-	57.4	-	39.6	-	354.6
PP/PCL 80/20	15.0	-48.6	2.1840	162.8	54.0	40.4	5.1	408.3	351.6
PP/PCL/nTiO ₂ 80/20/5	14.4	-50.4	2.3620	162.8	54.0	36.5	6.3	409.2	350.8
PP/PCL/nTiO ₂ 80/20/5 UV	16.8	-45.0	1.2070	162.1	51.0	36.4	5.5	402.7	350.0
PP/PCL 50/50	13.5	-51.3	2.3200	162.9	55.2	35.5	10.4	414.7	353.5
PP/PCL/nTiO ₂ 50/50/5	14.1	-51.9	1.2600	161.9	55.2	23.5	14.4	423.0	354.4
PP/PCL/nTiO ₂ 50/50/5 UV	10.4	-41.7	0.8819	160.3	52.7	27.5	18.9	415.4	356.9
PP/PCL 20/80	17.0	-45.4	1.4490	161.3	54.2	31.6	4.4	418.1	354.0
PP/PCL/nTiO ₂ 20/80/5	-	-47.8	0.8853	164.1	55.3	7.5	27.8	421.6	357.1
PP/PCL/nTiO ₂ 20/80/5 UV	-2.4	-36.8	0.7289	161.6	54.3	9.4	37.3	427.1	358.3

During thermal decomposition the TG curves display a two stage decomposition process for all samples before and after UV irradiation. The first step corresponding to the decomposition of PCL i.e. chain scission of the ester (C = O) group with T_{onset} of 354.6 °C while the second step corresponds to the chain scission of PP matrix with T_{onset} of 420.2°C. The values of T_{onset} indicate that the initial decomposition reaction for PP begins at higher temperature than for PCL. Thus, it may be concluded that the unirradiated PP polymer is more stable against thermal decomposition than the unirradiated PCL. It can be seen from **Table 1** that T_{onset} increases by the addition of nTiO₂ in blends. Therefore, it can be concluded that TiO₂ enhance the thermal

stability of PP/PCL blends. From **Table 1**, it was shown that the thermal stability of PP/PCL blends increases with increasing the ratio of PCL for the unirradiated and irradiated blends. Also, the thermal stability of irradiated PP/PCL blends with all its compositions are thermally stable than those of unirradiated. This behaviour is due to the formation of a crosslinked structure localised at the surface of the PCL during UV irradiation. As expected, the formation of irradiation induced crosslink has improved the thermal stability of irradiated PP/PCL blends.

CONCLUSION

A modification of no biodegradable synthetic polymers by a biodegradable polymer is producing environmentally friendly polymers. The main problem in modification of no biodegradable synthetic polymers with biodegradable polymers is compatibility between polymers mixtures with different properties. In order to investigate the aging process of PP/PCL blends without and with nTiO₂ filler with UV irradiation samples were subjected to accelerated aging. The obtained results show that the particles of nTiO₂ as filler in PP/PCL blends have the photocatalytic property and improves the photocatalytic degradation after UV irradiation. Furthermore, photodegradation process might occur through the chain scission reactions, crosslinking and consequently photocatalytic degradation of polymers. The thermal stability of irradiated PP/PCL blends with all its compositions are thermally more stable than those of unirradiated, this is due to crosslinking.

ACKNOWLEDGEMENTS

The authors wish to thank for the financial support the University of Zagreb, Croatia (grant no. 118009/2016).

REFERENCES

- [1] KROCHTA, J.M., DE MULDER JOHNSTON, C. Edible and biodegradable polymer films: Challenges and opportunities, *Food Technology*, 1997, vol. 51, no. 2, pp.61-74.
- [2] WOODRUFF, MARIA A., HUTMACHER, DIETMAR W. The return of a forgotten polymer: Polycaprolactone in the 21st century. *Progress in Polymer Science*, 2010, vol. 35, no.10, pp. 1217-1256.
- [3] V.R. SINHA, K.BANSAL,R.KAUSHIK, R.KUMRIA, A.TREHAN, Poly-ε-caprolactone microspheres and nanospheres, an overview., *International Journal of Pharmaceutics*, 2004,vol. 278,no.1,pp. 1-23.
- [4] SAADOUN M, CHORFI H, BOUSSELMI L, BESSAĐS B. Polymer supported porous TiO₂: application to photocatalysis. *Physica Status Solidi (C)*. 2007, vol. 4, no.6, pp.2029-2033.
- [5] TSUJI H, ISHIZAKA T., Porous biodegradable polyesters, 3. preparation of porous poly(ε-caprolactone) films from blends by selective enzymatic removal of poly (l-lactide). *Macromolecular Bioscience*. 2001, vol.1,no.2,pp.59-65.
- [6] WUNDERLICH, B. *Macromolecular Physics*, Vol. 3, *Crystal Melting*, Academic Press, New York 1980.
- [7] KOENING, M.F. ,HOUANG, S.J. Biodegradable blends and composites of polycaprolactone and starch derivatives, *Polymer*, 1995, vol. 36, no.9, pp. 1877-1882.
- [8] BOYD, R. H. Relaxation processes in crystalline polymers: experimental behaviour - a review, *Polymer*, 1985, vol.26, no.3, 323-347.