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Impact of the ZnO concentration on the thermal endurance, biodegradation rate and hydrophilicity of a PCL/ZnO nanocomposite

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INTRODUCTION

Nowadays, the use of polymeric based materials is surrounded by controversy, with media showing images of animals entangled in fishing nets, dead due to ingestion of plastics, debris polluting beaches etc. One way to address this problem is through the use of biodegradable plastics, but many polymers in this class present subpar mechanical and thermal properties when compared to commodities and need intense use of additives, many of them containing aromatic components that can be even more harmful than large pieces of plastic. An alternative that could replace part of these additives on a biodegradable polymer was here proposed.

Polycaprolactone (PCL) was chosen as a polymeric matrix due to its good mechanical properties and rapid biodegradation. Nano ZnO was selected as additive due to its UV filter and antimicrobial properties, which counterbalances a strong reduction on the thermal endurance of the polymeric matrix, allowing a good degree of control of the degradation process of the polymer, aiming to not prolong its residence time after being discarded, whilst providing antimicrobial protection during its lifespan.

EXPERIMENTAL

The concentration of ZnO (US Research Nanomaterials, 10-30 nm) was varied from 1 to 10% wt. in order to assess how it impacts on thermal endurance, biodegradation and contact angle properties of a PCL (Perstorp Capa 6500) based nanocomposite (NC). To the nanoparticles, after being vacuum dried and ultrasonicated in chloroform, a PCL-co-aPC (aliphatic polycarbonate) wax (Perstorp Capa 7203), in a ratio of 1.5 to 1 part of ZnO, was added in order to create an interphase between nanoparticles and the PCL matrix, preventing aggregation during film casting, when PCL is added. This methodology proved efficient, as SEM micrographs show little aggregation of nano oxide. To assess thermal endurance, Toop method [1] was used and Ozawa/Flynn/Wall (OFW) [2] and/or Broido [3] methods were used for obtaining the activation energy, when possible. Biodegradation essays were made on a simulated soil, according to ASTM G160 standard.

Hydrophilicity of the samples was assessed through water uptake measurements, whose residence time of the samples was 1 week.

RESULTS AND DISCUSSION

When compared to the control, NCs had a slower biodegradation rate as ZnO concentration increased, preserving the smoothness of the film surface for a longer period of time, whilst PCL films started to show roughness and even small holes on the surface, indicating biodegradation, as shown in Fig 1.

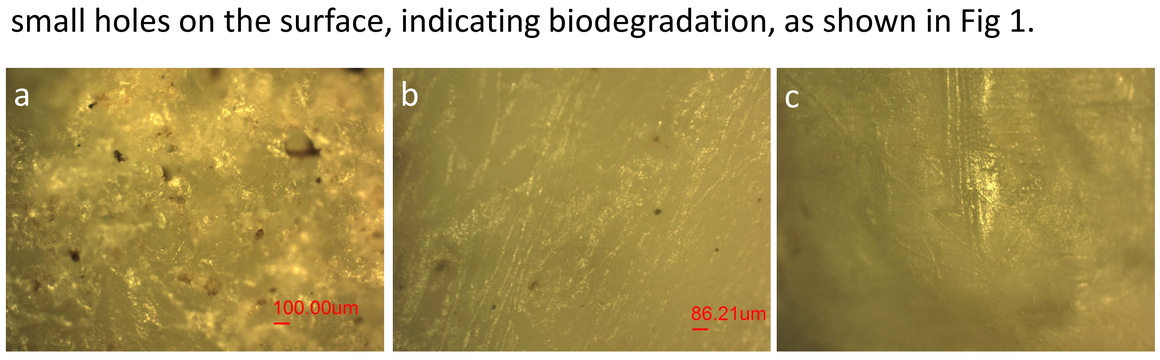

Fig. 1 – Optical micrographs of the surface of PCL and NC films subject to 1 month of biodegradation. a: PCL; b: 1% ZnO; c: 3% ZnO.

Water uptake and contact angle measurements indicated that the NCs exhibited a much more hydrophilic behavior than the PCL, an usually hydrophobic polymer. PCL has virtually not absorbed any water during the 1 week period of the experiment . On the other hand, 1% ZnO NC has shown a strong increase on its mass, whilst 3% ZnO NC has shown a small decrease to its mass, indicating the occurrence of some kind of degradation process, probably hydrolysis, but further investigation is necessary on this subject. Data is in Table 1.

Table 1 – Mass variation of the samples after one week immerse in water

Material	Dm (%)
PCL	-
1% ZnO	+11.15
3% ZnO	-0.4

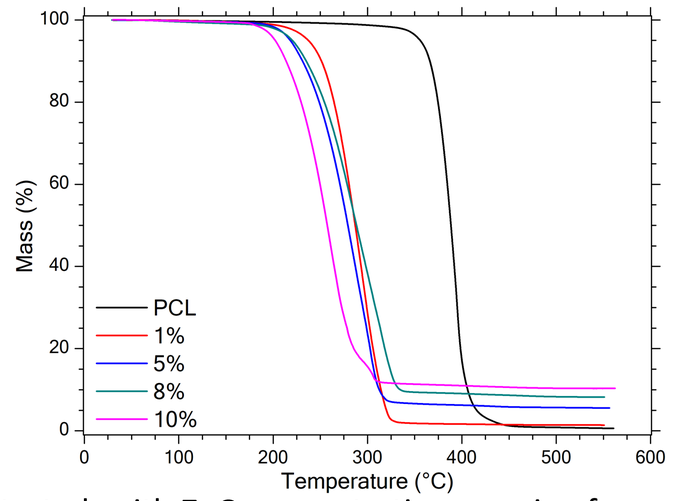

Fig 2 – TG curves of the samples tested, with ZnO concentrations varying from 0 to 10% wt.

Thermogravimetry showed a strong reduction on the onset temperature of mass loss, reducing it by around 100 °C on NCs, as shown in Fig 2. This reduction is usually attributed to transesterification and or depolymerization induced in the polymeric matrix by ZnO at temperatures above 220°C [4].

Due to the reduction observed on the thermal endurance, activation energy for thermal degradation has also showed a strong reduction, resulting in a decrease of several orders of magnitude on the estimated lifetime of the materials, from periods as long as the age of universe to periods of a few years at ambient temperature. Hence, it is important to remember that these periods of degradation are estimated based only on thermal degradation, disregarding ant other forms of degradation. TG data, including activation energy, is in Table 2

Table 2 – TG data, including activation energy (E_a), calculated by Broido (BR) or OFW methods, and estimated thermal endurance (t_d).

Material	T_{onset} (°C)	10% mass loss (°C)	DTG_{max} (°C)	E_a (kJ/mol)	t_f (h, 25°C)	t_f (h, 100°C)
PCL	364.7	366.0	395.3	197(OFW)/ 229 (BR)	1.55E17/ 6.3E22	1.7E10/ 5.3E14
1% ZnO	253.0	251.2	291.1	122.8 (BR)	9.1E7	4328
5% ZnO	233.8	231.1	303.5	85.2 (BR)	64480	65
8% ZnO	240.5	235.0	314.7	82.8 (BR)	34107	41
10% ZnO	220.8	213.7	257.3	86.3 (BR)	58460	52

Data in the table indicate that, probably, occurred some aggregation of the ZnO particles above the concentration of 8% wt. of ZnO, consequently reducing the contact area between the two phases, slowing down the expected degradation mechanism aforementioned, given the increase in E_a that was observed.

CONCLUSIONS

Results showed that is possible to control thermal endurance, biodegradation rate and hydrophilicity of a PCL/ZnO NC according to the concentration of nano ZnO used, and the resulting product still presents an adequate lifespan for the consumer, while not prolonging its residence time in the environment.

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