Thermal and Mechanical Properties of Isotactic Polypropylene/TiO_2 Particulate Composites

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Dedicated to the Occasion of the 80th Birthday of Prof. HUANG Bao-Tong and Prof. FENG Zhi-Liu

Abstract Particulate composites based on isotactic polypropylene(iPP) and titanium dioxide (TiO_2) have been prepared and their morphology and thermal behavior investigated by scanning electron microscopy (SEM), differential scanning calorimetry (DSC) and thermogravimetric analysis(TGA). Tensile tests were performed to assess the influence of TiO_2 on the mechanical properties of the iPP.

Keywords iPP/TiO_2 composite, packaging film thermal property, mechanial property
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It has been recently demonstrated that titanium dioxide possesses photocatalytic action in the decomposition of ethylene to carbon dioxide and water in the presence of atmospheric oxygen[1~3]. TiO_2, a largely produced substance exploited in many industrial sectors, is used as an additive in cosmetics and even in some food, because of its very low toxicity level. Furthermore, TiO_2 shows absorption properties that can avoid water condensation on the interior surface of packages in the presence of high humidity. The incorporation of TiO_2 in polymers has been carried out in order to increase the refractive index of materials and hence to confer opacity[4]. In the light of all the peculiarities of TiO_2, and especially because of its antagonism toward ethylene, a new application of TiO_2 in packaging materials for agricultural produces is suggested. Isotactic polypropylene is one of the most widely used polymers in packaging of agricultural products. The relatively high gas permeability of iPP, compared to other polymers, can still be insufficient for the packaging of vegetables. Indeed the accumulation in a package of ethylene, a final product of the metabolism of fresh vegetables, induces over-ripening and deterioration. Therefore the incorporation of an inorganic substance like TiO_2 in a polyolefin could result in a high performance packaging material, combining photocatalytic property and enhanced gas permeability[5].

This work presents a preliminary characterization of the iPP/TiO_2 particulate composites with the emphasis on the investigation of their morphology and thermal and mechanical properties.

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1 Experimental Part

1.1 Materials

An isotactic polypropylene(iPP), melt flow index 9.5 dg/min, containing 2.4% of ethylene units randomly distributed along the chain, was provided by Montell.

TiO_2 in rutile crystalline modification, density 4.0 g/cm^3, covered with a polysiloxane agent, was provided by Kronos International, Inc.

1.2 Mixing procedure and specimen preparation

The iPP and TiO_2 in mass ratios m(iPP)/m(TiO_2) 100/0, 99/1, 95/5, 90/10 and 80/20, were mixed in a Brabender apparatus for 10 min at 215℃, rising gradually the mechanical moment up to 32 r/min.

The materials were compression-molded in a press at 200℃ for 5 min without applied pressure to allow complete melting. A pressure of 3.8×10^5 Pa was then applied for 5 min and the samples were quenched with water, then the pressure was released.

Samples cut from the parallelepiped shaped sheets with a thickness of 1.5 mm were used for scanning electron microscopy, differential scanning calorimetry, thermogravimetry, optical microscopy and mechanical tensile experiments.

1.3 Thermogravimetry and differential scanning calorimetry

Thermogravimetrical analysis of the samples was performed under nitrogen atmosphere with a TC 10A Mettler instrument equipped with a M3 analytical thermobalance by heating each sample from 40 to 600℃ at a rate of 5℃/min.

Thermal analysis was performed with a Mettler TA-3000 differential scanning calorimeter, calibrated with pure indium, lead and zinc standards at various scanning rates, and purged with dry nitrogen gas through the cell at a flow rate of 20 mL/min.

To determine the glass transition temperature(T_g) the samples were submitted to the following thermal program: heated from -60 to 200℃ at 20℃/min, cooled from 200 to -60℃ at 50℃/min and reheated from -60 to 200℃ at 20℃/min.

The T_g was determined as the maximum of the peak by applying the first derivative procedure(included in the Mettler software) to the last run.

To determine the fusion and crystallization enthalpies(ΔH_m and ΔH_c), the samples were heated from 30 to 250℃ at 10℃/min and then cooled to 30℃ at 10℃/min. The observed melting and crystallization temperatures(T_m and T_c) were obtained from the maxima of the endothermic or exothermic peaks. The crystallinity of the iPP phase(X_c) was calculated from the melting curves by the formula:

$$X_c = \Delta H_m / \Delta H_m^0$$

where ΔH_m^0 is the enthalpy of melting per gram 100% crystalline iPP(210 J/g)[6] and ΔH_m the measured enthalpy of melting per gram iPP.

1.4 Mechanical tensile tests

Stress-strain curves were obtained according to ASTM D256 at a cross-head speed

of 20 mm/min. Modulus and stress and strain at rupture were calculated from such curves on the average of 6 specimens.

1.5 Scanning electron microscopy

The surface analyses were performed by using a SEM Philips XL 20 Series microscope on cryogenically fractured surfaces, coated with Au–Pd alloy with SEM coating device(SEM Coating Unit E5150, Polaron Equipment Ltd.).

2 Results and Discussion

Scanning electron microscopy analyses of the cryogenically fractured surfaces of iPP/TiO_2 compression molded samples are shown in Fig. 1. The micrograph of the 95/5 composite (Fig. 1*a*) reveals the presence of small TiO_2 granules homogeneously distributed in the iPP matrix. The dispersed particles are roughly spherical with an

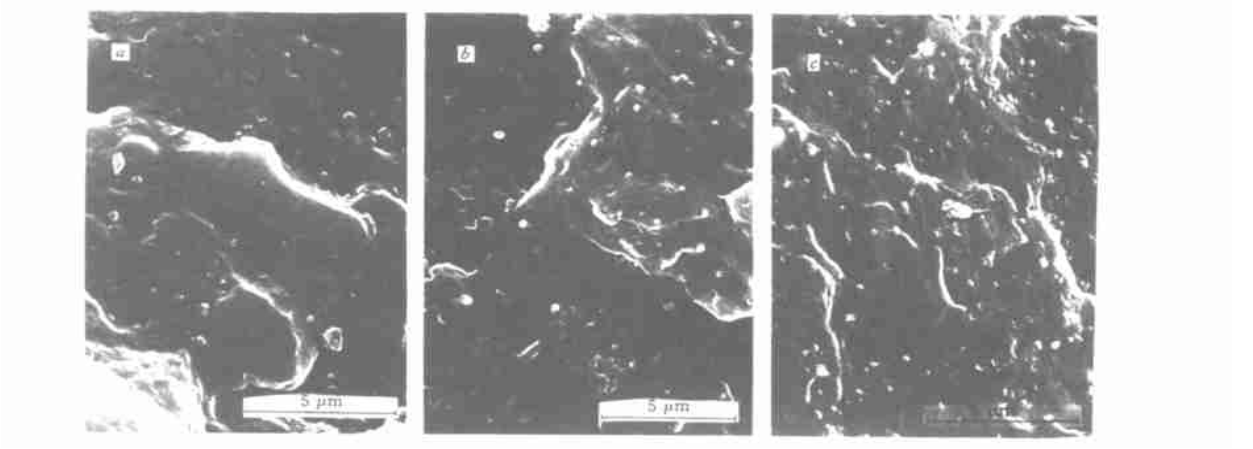


Fig. 1 Electron micrographs of iPP/TiO_2 samples
m(iPP) /m(TiO_2): *a*. 95/5; *b*. 90/10; *c*. 80/20

average diameter of about 0.3μm. A larger number of dispersed domains are obviously present in samples containing higher amounts of titanium dioxide, as shown in Fig. 1*b* and 1*c*. For all the samples the uniformly distributed TiO_2 particles are well welded to the polypropylene matrix, indicating the achievement of good dispersion as well as high adhesion level between the filler and the matrix.

The thermal stability of iPP and iPP/TiO_2 composites was analyzed by thermogravimetry. The thermoanalytical curves representing the percentage of mass loss of the samples as a function of temperature are shown in Fig. 2. The values of the degradation temperature $T_{0.5}$ corresponding to a

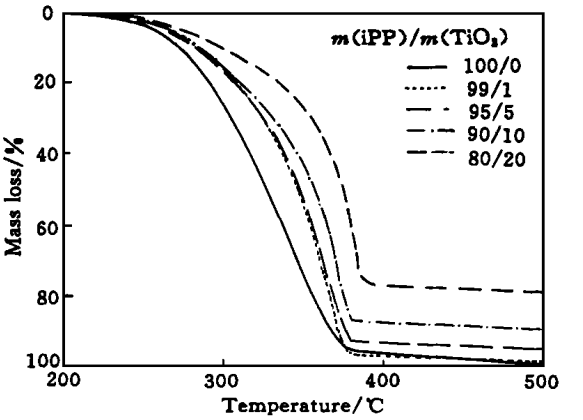


Fig. 2 Therogravimetrical curves of iPP/TiO_2 samples

mass loss of 50% are reported in Tab. 1. Up to about 230℃ all the specimens are rather stable and almost no mass loss can be detected. Although the range of degradation temperature (230~ 380℃) is independent of composition and the addition of TiO_2 does not shift the onset of mass loss to higher temperatures, the mass of the composites drops with a steepness lower than that of the neat iPP, indicating an increase of thermal stability of iPP in the presence of TiO_2.

Tab. 1 Degradation temperature of iPP/TiO_2

m(iPP) /m(TiO_2)	100/0	99/1	95/5	90/10	80/20
$T_{0.5}$ /℃	325	345	348	353	378

The T_g, T_m, T_c, ΔH_m, ΔH_c and X_c values are shown in Tab. 2. The data indicate that the crystallinity level of the polypropylene matrix as well as the glass transition temperature are almost unaffected by the presence of TiO_2. This findings well conform to the suggested final use of iPP/TiO_2 composites in packaging high respiration food. Indeed, an increase in crystallinity, or a reduction of the chain flexibility of iPP in the presence of TiO_2, might enhance the resistance to gas solubilization and diffusion through films, thus compromising their use as poor gas-barrier materials.

Tab. 2 Thermal parameters of iPP/TiO_2 composites

m(iPP) /m(TiO_2)	T_g /℃	ΔH_m /(J·g^{-1})	I_c /%	T_m /℃	ΔH_c /(J·g^{-1})	T_c /℃
100/0	- 5	55	29	154	56	98
99/1	- 5	61	32	154	60	99
95/5	- 5	61	32	153	62	100
90/10	- 5	60	31	155	58	98
80/20	- 5	61	32	154	61	102

Optical microscopy observations were possible only on plain iPP and on the composite containing 1% of TiO_2, since samples with higher TiO_2 contents have too poor transparency to be observed by light transmission microscopy. The comparison between dynamically crystallized samples of iPP/TiO_2 99/1 and 100/0 revealed no significant difference in nucleation density. Therefore iPP shows the same fine texture independent of the presence of TiO_2 particles, at least at low TiO_2 content. The similar values of T_m, ΔH_m, T_c and ΔH_c among all the composites also suggest that they present a similar behaviour concenning nucleation and growth rates of iPP spherulites, which should retain their average dimension and morphology in the presence of TiO_2.

Tensile tests demonstrate that, when the TiO_2 percentage is $\leq$ 5%, there is an increase in elongation at break, as shown in Tab. 3, probably because of the hydrophilic nature of TiO_2 particles and/or their uniform distribution within the matrix. It is worth while to underline that this increase is neither accompanied by a diminution of the stress at break nor by a reduction of the Young's modulus.

Tab. 3 Mechanical parameters of iPP/TiO_2 composites

m(iPP) /*m*(TiO_2)	σ_b /MPa	χ_b /%	*E* /MPa	*m*(iPP) /*m*(TiO_2)	σ_b /MPa	χ_b /%	*E* /MPa
100/0	32	280	1 100	90/10	32	17	1 200
99/1	32	390	1 100	80/20	32	14	1 300
95/5	32	380	1 100				

Higher percentage of TiO_2 produces an increase in elastic modulus and simultaneous decrease in elongation at break, although no influence on the breaking strength is observed.

3 Conclusion

The present study on thermal and mechanical properties of iPP/TiO_2 particulate composites shows that they are suitable for prospective flexible film for packaging of agricultural produces in the light of the absorbing ability, and photocatalytic property toward ethylene degradation and expected increased gas permeability due to the presence of TiO_2.

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