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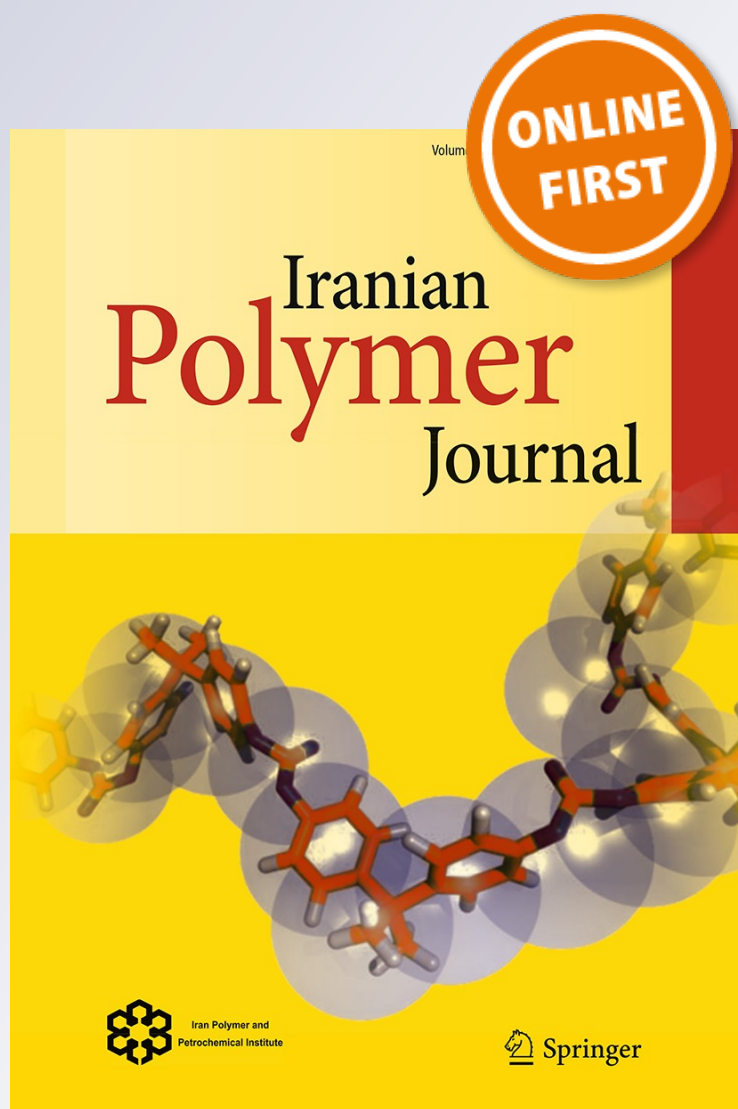
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Lemon essential oil desorption from polypropylene/talc nanocomposite films

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Abstract A phenomenological analysis on desorption mechanism of lemon essential oil in semicrystalline polymer nanocomposites is performed. Films were made of polypropylene and talc nanoparticles obtained by blown extrusion were used as a case study due to the high complexity of sorption phenomena in such systems containing a semicrystalline polymer and nucleating particles. In this sense, a systematic analysis combining both morphological effects and intrinsic properties of each component was considered. Talc characteristics, e.g., morphology, surface chemistry, oil absorption properties, mean particle size and its distribution, and impurity presence, were considered in desorption analysis. Regarding semicrystalline matrix, morphological and crystalline changes induced by talc nanoparticles and processing were included in this study. Desorption of lemon essential oil from nanocomposite films with different talc concentrations (0, 1, and 5 wt%) which have distinctive and well characterized morphologies was evaluated through gravimetric and thermogravimetric analysis. Results show that polypropylene film has a desorption rate higher than nanocomposites containing 5 wt%, but lower than those with 1 wt% talc. This behavior is a consequence of the global crystallinity configuration changes produced by nanoparticle concentration and film obtaining process. It is revealed that simplified and conventional approaches that consider tortuosity as unique effect of particle presence in nanocomposite mass transport do not allow to comprehend the desorption mechanism involved in a complex system such as the semicrystalline polymer

nanocomposites. The present study gives additional insight into the complex mechanism involved in desorption of strongly swelling oil in nanocomposite films based on semicrystalline polymers and mineral nucleating particles.

Keywords Nanocomposite · Polypropylene · Talc · Desorption mechanism · Semicrystalline matrix · Particle nucleation

Introduction

In recent years, the development of packaging using polymer films has experienced a continuous and accelerated growth. This is due to the consumer demand and better benefits that this kind of materials offers in contrast with the conventional ones [1].

Particularly, to satisfy the increasing consumer expectations, packaging must be safe, inexpensive, and durable enough to assure proper product shelf life, quality, and sensorial attributes [2]. Besides protecting and preserving product during storage and distribution, packaging is the main responsible for sorption and release of aromas, being these the factors that define the acceptability of a packaged product [3]. In this regard, aroma incorporation into packaging material can be used to improve product quality to attract consumer and/or to balance any detrimental effects of aroma loss [4]. Thus, polymer could release aroma on the store shelf to strengthen this sensorial attribute of the packaged product, compensating losses during its shelf life.

Generally, natural or synthetic essential oils are used as fragrance bases, flavor, and bioactive agents [5]. When they are incorporated into a packaging material, a controlled release of these volatile molecules is required [6].

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In general, aroma diffusion depends on polymer physicochemical properties, flavor molecules as well as external conditions [7]. Regarding to the aroma, its chemical composition, concentration, volatile components, and polarity are crucial aspects on the release. Meanwhile, its solubility in the packaging material may be affected by external factors like storage time or relative humidity.

Polypropylene (PP) is one of the polyolefin most commonly used in packaging field due to its good final properties, easy processing, and relatively low cost [8]. However, aroma retention in films based on PP is quite low because of its high chemical inertness. For this reason, the increase of aroma sorption capacity of PP becomes an interesting issue, which would extend the applications of this polymer in packaging field.

One alternative is to use PP films filled with mineral nanoparticles to control the aroma release. In this regard, particles would retard the volatile molecule diffusion in nanocomposites [9]. Moreover, films based on PP and mineral nanoparticles as packaging materials are advantageous because it is possible to tailor their final properties for a particular application [10]. Thus, to develop polymer nanocomposite films with tailored properties at low cost results very attractive to extend the use of these materials in packaging field. Particularly, nanocomposites based on PP and talc have combined good properties with economic advantages.

Talc is considered a good reinforcement for semicrystalline polymer matrices due to its low cost and convenient platy particle morphology that enhances degree of crystallinity [11]. This mineral is a magnesium silicate with an ideal chemical formula of $Mg_3Si_4O_{10}(OH)_2$ which is widely used in industry as an absorbent agent [12, 13]. Particularly, talc nanoparticles with micron-sized dimensions on length and width, and nanometric thicknesses induce crystal nucleation and enhance degree of crystallinity and macromolecular orientation, improving mechanical properties of PP [14, 15].

Concerning to the aroma diffusion mechanism, the simplest models for polymer films are based on Second Fick's Law. This approach considers that: (1) equilibrium at the film surface is reached immediately, (2) mass transfer occurs only in the film thickness direction and (3) polymer behaves as a homogeneous phase. This set of hypotheses is valid only for amorphous polymers when sample thickness is negligible compared to other two dimensions.

In the particular case of semicrystalline polymers, the basic assumption reported in literature is that the crystals consist of an impermeable phase and the diffusion occurs only in the amorphous phase. It is supposed that crystals act as physical barriers to the penetrating molecules, forcing them to follow longer paths and increasing the tortuosity.

Additionally, polymer crystals can immobilize side-chains in the amorphous phase, reducing its free volume [16]. For nanocomposite films, Choudalakis et al. [16] reported that theoretical approaches related to the diffusion phenomenon consider that these materials are constituted by a permeable phase (polymer matrix) with non-permeable nanoparticles which are well dispersed and distributed. In this regard, aspect ratio, concentration, and orientation of nanoparticles are taken into account as main factors influencing the mass transfer. However, aroma diffusion is restricted to the polymer matrix. This phenomenon is usually modeled using Fick's law, considering the matrix as pure polymer that conserves its original properties. This model gives a good approximation for amorphous matrix nanocomposites, but several factors should be taken into account for semicrystalline matrix nanocomposites.

Particularly, diffusion mechanism in PP/talc blown films requires a systematic phenomenological analysis as a result of their complex morphologies. These materials present a preferential orientation of mineral nanoparticles and polymer crystals induced by blow extrusion processing. Films based on PP/talc nanocomposites involve a semicrystalline matrix containing strong nucleating nanoparticles, then, PP crystals grow onto talc surfaces up to found another crystal.

As it was demonstrated in a previous work [15] when 1 wt% talc is included, PP crystal growth is not impeded by other ones. Then, final morphology of nanocomposite films includes crystalline entities separated by net amorphous phases. On the opposite, in nanocomposites containing 5 wt% talc, due to the presence of great amounts of nucleation sites, crystal growth on a particle is strongly impinged by the other crystals developed on the neighboring nuclei. As a consequence, an "interpenetrating" crystal morphology without net amorphous "inter-crystal" zones is achieved. Thus, the overall crystalline configuration and final morphology of PP/talc nanocomposite depend on particle concentration, strongly affecting diffusion mechanism.

On the other hand, essential oils commonly used in packaging applications allow the introduction of more than one functionality, e.g., aroma and biocidal activity. In this way, lemon essential oil is one of the most used since this substance is "Generally Recognized As Safe" (GRAS) by the Food and Drug Administration (FDA). This attribute allows that oil impregnated films can be used for applications in contact with food, beverages, pharmaceuticals, as well as, in products of cleaning and health care. This oil is a strongly swelling agent for PP including an additional factor in the complexity of the aroma desorption from PP/talc films [17].

The aim of this work is to perform an accurate phenomenological analysis related to the sorption mechanism of lemon essential oil in blown nanocomposite films from

Table 1 Lemon essential oil composition

| Component | Percentage (%) |
|---------------------|----------------|
| Limonene | 67.83 |
| β -Pinene | 15.61 |
| α -Terpinene | 8.50 |
| α -Pinene | 2.33 |
| β -Mircene | 1.51 |
| α -Citral | 1.41 |
| β -Citral | 0.96 |
| Terpinolene | 0.37 |
| Not identified | 1.48 |

PP, a semicrystalline matrix, and talc nanoparticles. A systematic analysis including both morphological effects and intrinsic properties of each component is considered. Also, talc effect in nanocomposites with 0, 1, and 5 wt% on polymer crystallization is analyzed, at the same time the induction of nanoparticles and crystal orientation by blow process on diffusion mechanism is considered.

Experimental

Materials

Commercial PP Cuyolen, kindly supplied by Petroquímica Cuyo (Argentina), was used as polymer matrix (melt flow index: 1.8 g/10 min, M_w : 303,000 g/mol, M_w/M_n : 4.45). To improve the compounding with talc nanoparticles, PP pellets were grinded up to particles with an average size of 1700 μ m. Australian talc (A10) with a purity degree of 98 wt% was used in the present study. This mineral sample was provided by Dolomita S.A.I.C (Argentina). Previous studies have enabled to describe the microcrystalline structure of this talc, consisting of rounded and pseudo-spherical shape of particle aggregates [14]. As aroma, lemon essential oil, obtained by cold pressing of lemons from Tucuman (Argentina) was used to impregnate PP and nanocomposite films. The essential oil composition obtained by chromatography analysis is shown in Table 1 [18].

Nanocomposite film processing

A Goettfert counter-rotating twin screw extruder (Germany; $D = 30$ mm, $L/D = 25$) with a cylindrical die (1 mm) and a screw velocity of 30 rpm was used for PP/talc compounding by melt extrusion. The barrel temperature profile from hopper to die was 170–190–200–210–220 °C and it was hold constant during processing. Then, composite was solidified by passing through a water bath and finally it was pelletized. Different talc concentrations were

used to prepare nanocomposites (0, 1, and 5 wt%) and they were named as PP (talc concentration) A10, i.e., PP1A10 and PP5A10.

Finally, PP/talc nanocomposite films were obtained in a Maqtor downward blow film machine at pilot scale (Argentina), which was designed for PP films. Blown film extruder was fed with pellets obtained in the compounding step. A temperature profile of 170–180–185–185 °C in the blow extruder and a cooling air temperature of 22 °C were used. The extruder screw rotation speed was 30 rpm, meanwhile the blowing ratio was set at 2.5. Nanocomposite films with a layflat width of 30 cm were obtained. Neither nanocomposite compounding nor blown film extrusion process induced thermo-oxidative degradation [19].

Characterization

SEM

Talc particles distribution in nanocomposite films was assessed by scanning electron microscopy (SEM) technique. Films were cryofractured by immersion in liquid nitrogen, mounted on bronze stubs and coated with a gold layer (~ 30 Å). An argon plasma metallizer (sputter coater PELCO 91000, USA) was used to increase the surface conductivity. Film cross-sections were observed in a JEOL JSM-35 CF electron microscope (Japan), with a secondary electron detector. Besides, talc particle size distribution was assessed by SEM using the aforementioned microscope. In this sense, several micrographs were processed, considering hundreds of particles using AnalySIS 2.1 (Soft-imaging Software GmbH).

TEM

To evaluate talc dispersion within polymeric matrix, nanocomposite films were observed by transmission electron microscopy (TEM) technique. In this sense, ultra-thin sections of nanocomposite films embedded in an epoxy resin were obtained using an ultra-microtome at cryogenic temperature. The ultra-microtome used was a Leica model Ultracut UCT (Austria) with cryo-attachment EM-FCS and diamond knives for cryogenic cutting. Ultra-thin sections were placed onto gold TEM grids and they were observed employing a JEOL 100 CX II transmission electron microscope (Japan).

Optical microscopy

Talc nanoparticle distribution within nanocomposite were qualitatively evaluated by optical microscopy (OM). Film samples were observed in transmission mode using a Karl Zeiss microscope (Germany) equipped with a Leica DFC

280 digital camera (Germany), ranging magnifications from 40× to 1600×.

DSC

Degree of crystallinity of developed films was determined by differential scanning calorimetry (DSC) using a Perkin Elmer Pyris I (USA) instrument. Thermal experiment was performed by heating from 30 °C to 220 °C at 10 °C/min rate. All runs were carried out under nitrogen atmosphere to minimize the oxidative degradation. Degree of crystallinity (X_c) was determined using the following equation:

$$X_c (\%) = \frac{\Delta H_m}{(1-w)\Delta H_m^0} \times 100, \quad (1)$$

where ΔH_m is the melting enthalpy, w represents talc weight fraction, and ΔH_m^0 is the theoretical melting enthalpy of 100 % crystalline PP (209 J/g) [20].

XRD

Crystalline structure and orientation degree of polymer crystals in blown films were analyzed by X-ray diffraction (XRD). In this sense, a Philips PW1710 X-ray diffractometer (The Netherlands) was used, which is provided with a tube, a copper anode, and a detector operating at 45 kV and 30 mA with 2θ ranging from 3° to 60°. To evaluate the relative degree of PP crystals orientation, the peak heights of two monoclinic reflections (040 and 110) were measured from X-ray diffraction spectra and the ratio of their intensities (I_{040}/I_{110}) was calculated, according to Rybnikar [21].

Desorption tests

Polypropylene and nanocomposite films were impregnated with lemon essential oil up to saturation before desorption experiments. For this purpose, film samples were immersed in the essential oil within closed caramel-colored container, until obtaining constant weight by successive measurements. This procedure was realized for all films at controlled temperature and relative humidity (25 °C and 60 % HR). Then, films were removed from the liquid phase and the oil exceeding on their surface was eliminated with a dry tissue, considering this step as the initial time. Measurements were performed by triplicate and the data were averaged.

Gravimetric method

Weight evolution during lemon essential oil desorption from PP and nanocomposite films were registered using an analytical balance model Mettler AE 163 (Switzerland). Samples were weighed at intervals of 1 min until no

variation was observed. Desorbed oil fraction was calculated as M_t/M_o , where M_t and M_o are the oil mass contained in the film at the time t and the mass of saturation (value at initial time), respectively.

TGA

Weight loss of impregnated films was determined at room temperature using a thermogravimetric balance (TA Instruments, Discovery Series, USA). Tests were carried out with a stream of oxygen. From this data, the lemon essential oil mass fraction was calculated.

Phenomenological analysis

Among factors that influence the sorption phenomena in semicrystalline polymers, the relative penetrant/polymer swelling, degree of crystallinity and crystalline morphology are the most relevant. The extent of polymer swelling is determined by its thermodynamic affinity or interaction with diffusing molecules [22]. When the affinity of the penetrant/polymer system is high, the amorphous regions within the polymer network tend to swell. This behavior is observed for lemon essential oil which is a relative strongly swelling agent for PP [17]. Besides, solubility of lemon oil in this polymer is favored as both molecules have apolar character.

The presence of polymer crystals also affects desorption of essential oil molecules. Crystals were considered as impermeable phases to penetrating molecules in the first approximations used in diffusion models. In this sense, when essential oil molecules enter into the polymer, thermodynamic swelling of amorphous regions occurs. At once, crystalline regions restrict the mobility of polymeric chains, influencing on the free volume available to the molecules diffusion in amorphous regions. Consequently, amorphous domains push against the crystals, originating stresses such that the resulting strains tend to cancel the thermodynamic swelling [23]. Particularly, this aspect is important in matrices based on PP, which can achieve degrees of crystallinity ranging from low values up to percentages higher than 50 %, depending on the processing method and experimental conditions.

Despite the hindrance of oil molecules diffusion by polymer crystals, their orientation induces a channeling phenomenon, establishing preferential paths within the polymeric matrix where oil molecules do not find any obstacles. Consequently, the amorphous regions are more accessible to penetrating molecules when polymer crystals are oriented.

Regarding nanocomposite films based on PP and talc nanoparticles, besides swelling as well as the presence

and orientation of crystals, another factors influence on the desorption of oil molecules. In this sense, inherent talc characteristics (morphology, surface chemistry, oil absorption properties, particle size, particle size distribution, and impurities presence) as well as particle dispersion and distribution and talc nucleating capability in polymeric matrix affect the transport of the essential oil molecules.

Generally, talc nanoparticles have a laminar morphology where elementary layers (0.66 nm thick) are disposed in a stacked arrangement, which are held together by weak Van der Waals forces with an inter-laminar distance of 0.18 nm [24]. This morphology allows obtaining a particle orientation in nanocomposite film which is strongly dependent on the processing method and conditions, giving an additional characteristic to the final product.

Talc particles have two kinds of surfaces, basal and edge ones, which are the responsible of conferring them an amphiphilic behavior. Basal surfaces present a strong hydrophobic character imparted by siloxane bonds (Si–O–Si). On the other hand, edge surfaces are hydrophilic due to Si–OH and Mg–OH groups, which are exposed by the mineral grinding. However, the predominant amount of basal surfaces (>90 % total surface) respect to edge ones determines the main hydrophobic character of talc particles [13]. This surface property favors a strong affinity between lemon essential oil molecules and talc particles. In this sense, basic hydroxyl groups present on talc mineral surface could interact with the acid groups of the essential oil molecules, promoting an acid–base interaction.

It is well recognized that pure talc can absorb oil between its platelets, reaching an absorption capacity of 80 mL/100 g [25]. Its use is reported as an industrial absorbent, mainly in the olive oil extraction, where a small quantity of talc is added to the olive paste to absorb the oil droplets.

Talc particle size and particle size distribution also influence the essential oil sorption in nanocomposite films. In this sense, a decrease in particle size produces an increase in talc surface area; meaning that the oil absorption should have a direct relationship with the specific surface area of talc particles. Additionally, particle size distribution is an important key to control the oil molecule's diffusion through nanocomposite film.

Regarding the presence of impurities, talc ore is composed by associated minerals, such as calcite (CaCO_3), dolomite [$\text{CaMg}(\text{CO}_3)_2$], magnesite (MgCO_3), and chlorite (Al–Mg–silicate), among others. Then, after grinding rock, these associated minerals are present in the talc particles. Impurities could influence on the oil affinity, lowering oil absorption of talc particles because they have different morphologies and surface characteristics.

Concerning to the influence of nanocomposite film morphology, talc dispersion and distribution are important

factors that affect the lemon essential oil desorption. It is well known that particles affect directly the tortuosity, forcing penetrant molecules to travel around them [26–28]. Also, oil molecules absorbed in talc particles must be released from them. It is important to consider that talc presence induces polymer chain alignment or alignment and modification of polymer crystals [29]. Talc nanoparticles have an efficient nucleating capability, besides acting as strengthening agents. Several works have demonstrated the role of talc on inducing PP crystallization, claiming that the alignment of few polymer chains on particle's basal surfaces allows the formation of nucleus during crystallization [11]. As a consequence, the growth of PP crystals is oriented into a particular direction, which is related to the epitaxial crystal growth on talc basal surfaces [14].

Taking into account the aforementioned factors, when PP/talc nanocomposite films are impregnated with lemon essential oil up to saturation, penetrant molecules remain absorbed in talc particles and swell the polymeric matrix. Then, during desorption process, oil molecules retained in particles must be released up to their surface, throughout the epitaxial crystal layer around particles to reach the polymeric bulk. It is important to highlight that polymeric crystals are generated from chain folding, but also contain amorphous zones. From this point, the desorption mechanism is similar to oil molecules located in polymeric matrix. Main factors that influence the penetrant path to film surface within matrix includes the tortuosity proceeding from both particles themselves and crystallinity increment as well as the path from inter-crystal amorphous zone. These aspects vary with the amount and size of the talc particles, as well as, their dispersion and distribution in the film. Thus, a complex mechanism is involved in lemon essential oil desorption from nanocomposite films containing a semicrystalline matrix and talc nanoparticles. In this way, the present study is focused on the several factors related to particles and polymer characteristics, as well as, their specific interaction.

Results and discussion

Characterization

In this section, results of a detailed characterization of talc nanoparticles as well as of PP and nanocomposite blown films are presented. This was performed to understand whether the aforementioned variables influence on the mechanism of lemon essential oil desorption in the present system. Morphology, mean size, and size distribution of the talc particles were assessed and presented in Fig. 1. From SEM micrographs in Fig. 1a, small individual platelets can be observed, evidencing the microcrystalline morphology

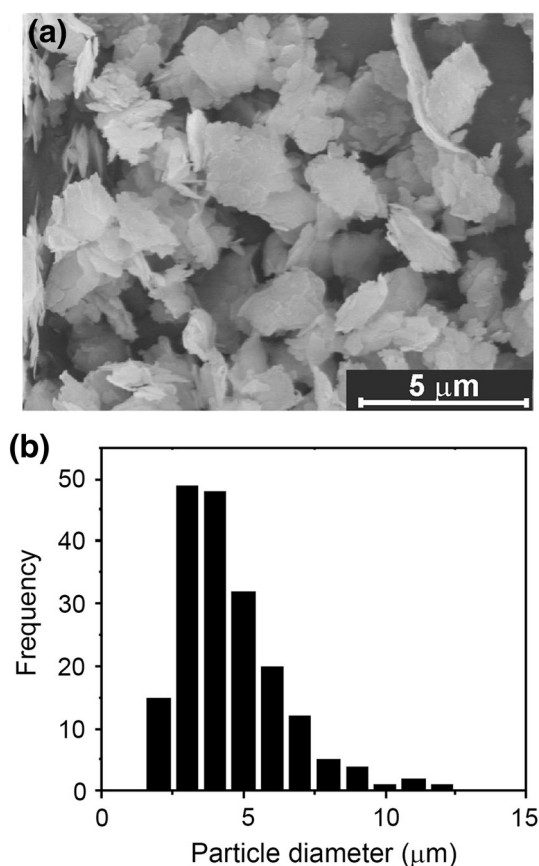


Fig. 1 a SEM micrograph and b number-weighted histogram of A10 talc nanoparticles

Table 2 Talc chemical composition

| Chemical composition | Percentage (%) |
|--------------------------------|----------------|
| SiO ₂ | 61 |
| MgO | 31 |
| Fe ₂ O ₃ | 1.1 |
| CaO | 0.30 |
| MnO | 0.10 |
| Al ₂ O ₃ | 0.9 |
| L.O.I. (1000 °C, 60 min) | 5.3 |

L.O.I. loss on ignition

of the talc nanoparticles, having micrometric basal surfaces and nanometric thicknesses [11]. The number-weighted histogram reveals that talc nanoparticles show a unimodal particle size distribution with a mean value at about 3.42 μm (Fig. 1b). Chemical analysis of talc sample is presented in Table 2. The high purity degree (98 wt%) of these particles, determined by mineralogical analysis, is corroborated comparing the chemical composition with the corresponding to a pure sample [30].

Macroscopically, blown films are homogenous and translucent without the presence of gels or foreign matter, as these would be readily visible in the final product. Taking into account that talc particles have micrometric basal surfaces and nanometric thicknesses, they are indistinguishable by sight, even though when films are examined through the light. Regardless talc concentration, the blown films had homogeneous thickness with a mean value for PP and nanocomposites around 50 ± 3 μm.

After a macroscopic evaluation, the microstructure analysis of blown films can provide useful information to explain the influence of talc nanoparticle's presence on the lemon essential oil release.

Figure 2 shows OM, SEM, and TEM micrographs corresponding to the surfaces, cross-sections, and ultra-thin section of blown films, respectively. In particular, PP shows a smooth and uniform surface (Fig. 2a, d, g) meanwhile talc particles, embedded in the polymeric matrix, can be clearly distinguished by OM and SEM in Fig. 2b, c, e, f, respectively. These mineral particles are well distributed within the matrix, evidencing a preferential orientation. In this sense, talc morphology and film processing favor this particle alignment where basal particle surfaces are placed parallel to that of the film, offering the less resistance to the flux during blow extrusion.

Particularly, talc dispersion in nanocomposite films was evaluated by TEM. Figure 2g–i shows representative TEM micrographs of the blown film morphology. Talc nanoparticles are clearly distinguished as darker lines in the lighter background (matrix). It is important to note that, due to the direction in which samples were ultra-microtomed, the section of particles that is exposed corresponds to their lateral surface. Nanocomposite films containing 1 wt% talc (Fig. 2h) show well-dispersed particles which have a mean lateral dimension of 60 nm. Meanwhile, when talc concentration is 5 wt%, thicker particles (~90 nm) are detected in Fig. 2i. Despite they are constituted by several talc platelets, they are still nanometric fillers due to their thicknesses. These results show that low particle concentration promotes an effective delamination of talc-stacked structure to favor its dispersion within the polymer matrix.

As it was described above, degree of crystallinity (X_c) and crystal orientation of polymer matrix also influence the lemon essential oil desorption from blown films. In this regard, X_c was determined by DSC considering that this technique allows to obtain a value that represents the bulk crystallinity, different from XRD which gives information about the degree of crystallinity at the film surface. PP orientation in all nanocomposite films was evaluated through the relative intensity between peaks corresponding to (040) and (110) planes ($I_{(040)}/I_{(110)}$) from XRD spectra. Each peak was assigned to the corresponding crystal and comparing to the data reported in the literature [31]. Table 3 shows

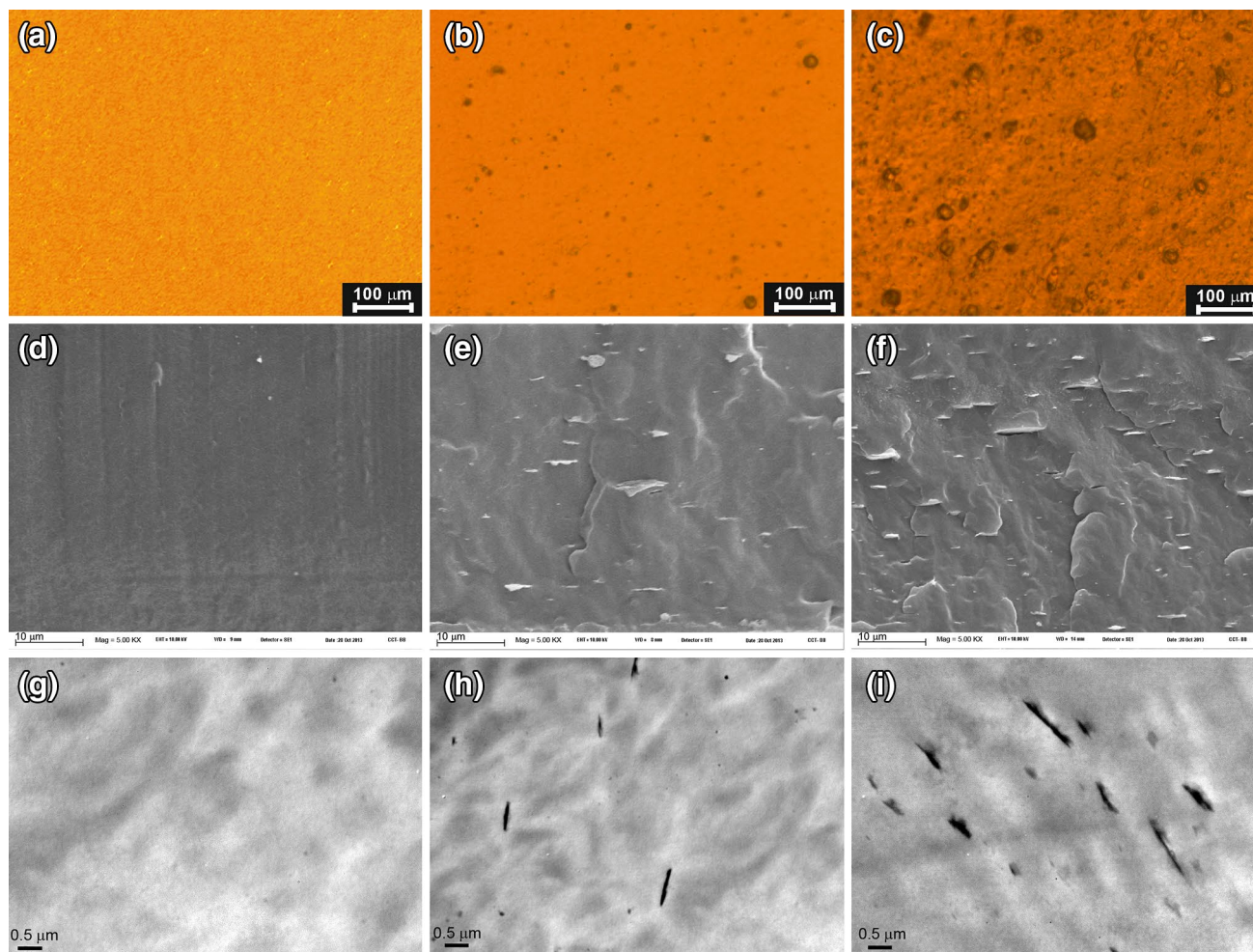


Fig. 2 OM micrographs of films surfaces: **a** PP, **b** PP1A10 and **c** PP5A10. SEM micrographs of film fractured surfaces: **d** PP, **e** PP1A10 and **f** PP5A10. TEM micrographs of film ultra-thin sections: **g** PP, **h** PP1A10 and **i** PP5A10

Table 3 Degree of crystallinity (X_c) obtained by DSC and ratio of diffraction peaks intensity ($I_{(040)}/I_{(110)}$) determined by XRD for PP and PP/talc nanocomposite films

| Sample code | X_c (%) | $I_{(040)}/I_{(110)}$ |
|-------------|-----------|-----------------------|
| PP | 40.7 | 12.2 |
| PP1A10 | 42.5 | 21.3 |
| PP5A10 | 43.0 | 18.0 |

degree of crystallinity as well as $I_{(040)}/I_{(110)}$ values for PP and nanocomposite films.

Nucleating efficiency of talc particles was evidenced on blown nanocomposite films, mainly at low concentration (1 wt%), where the change on X_c values is more notable. Particularly, a slight increment in the degree of crystallinity is observed for 5 wt% talc. This fact presumes that crystal growth begins to prevent the development of the neighboring crystals due to the increased presence of talc

nanoparticles. Concerning to $I_{(040)}/I_{(110)}$ ratio, several values are found in the literature for isotropic PP crystals. In this sense, Addink et al. [32] reported the value of 0.54, meanwhile Rybnikar [21] informed ratios comprised between 0.67 and 0.77 for injected PP/talc composites. The high values of $I_{(040)}/I_{(110)}$ ratio in Table 3 reveal a marked anisotropic crystalline morphology in all films as a consequence of blow extrusion process (biaxial orientation) and particularly, an additional contribution of talc particles in nanocomposite films. This anisotropic crystalline structure suggests a higher orientation of PP crystals. Thus, in these blown films, processing method and talc nanoparticle characteristics strongly influence on the morphology and orientation of PP crystals. An increasing tendency of $I_{(040)}/I_{(110)}$ ratio is observed when talc concentration raises, meaning that the crystal orientation is intensified by talc nanoparticles. However, this behavior is no longer valid for nanocomposites containing 5 wt% talc, where a decrease in $I_{(040)}/I_{(110)}$ ratio is observed. This result could be associated

to a restricted growth and orientation of crystals due to a more important presence of talc nanoparticles.

Desorption tests

To study the mechanism that governs the lemon essential oil desorption from blown nanocomposite films, gravimetric and thermogravimetric analysis were chosen to follow this phenomenon. Thus, desorption curves obtained from these complementary techniques were comparatively studied. Regarding this analysis, the influence of variables associated to inherent talc characteristics such as morphology, surface chemistry, oil absorption properties, and particle size were ignored due to the soleness of the talc sample used for all film formulations. Moreover, the narrow particle size distribution determined for A10 talc assured a homogenous desorption which facilitates the analysis of this mechanism. Additionally, the high purity degree allows considering the talc sample as a pure one, avoiding the effect of impurities in the essential oil desorption.

Desorption curves of lemon essential oil for PP and nanocomposite films, obtained by gravimetric and thermogravimetric analysis, are presented in Fig. 3. It is important to note that both normalized weight loss monitored by these techniques revealed consistent results, with a high reproducibility of the experiments. For all blown films it was observed a decreasing tendency, which was associated with the evolution of the essential oil desorption.

Figure 3 shows that desorption rate for nanocomposite containing 1 wt% (PP1A10) was faster than those of the other films. This result could be explained considering the different factors previously described in the phenomenological analysis of desorption from nanocomposite films. For this talc concentration, films present a less favorable thermodynamic swelling by lemon essential oil than PP due to talc nanoparticles act as anchor points, restricting the mobility of polymeric chains. On the other hand, the incorporation of 1 wt% nanoparticles contributes to a relative high increment of degree of crystallinity, according to the values reported in Table 3. Thus, despite the less favorable swelling and increased crystallinity in PP1A10 which would lead to a delayed oil desorption compared to PP film, the obtained results for both techniques are the opposite (Fig. 3).

Concerning to the oil absorption by talc, general knowledge related to this issue affirms that essential oils do not penetrate into talc particles. This assumption is based on the polymer crystal's growth at mineral surface, due to talc nucleating capability, which represents an impermeable obstacle to oil molecules. However, this is not completely true due to crystals are separated by amorphous phase where the "tie-chain molecules" act as connecting

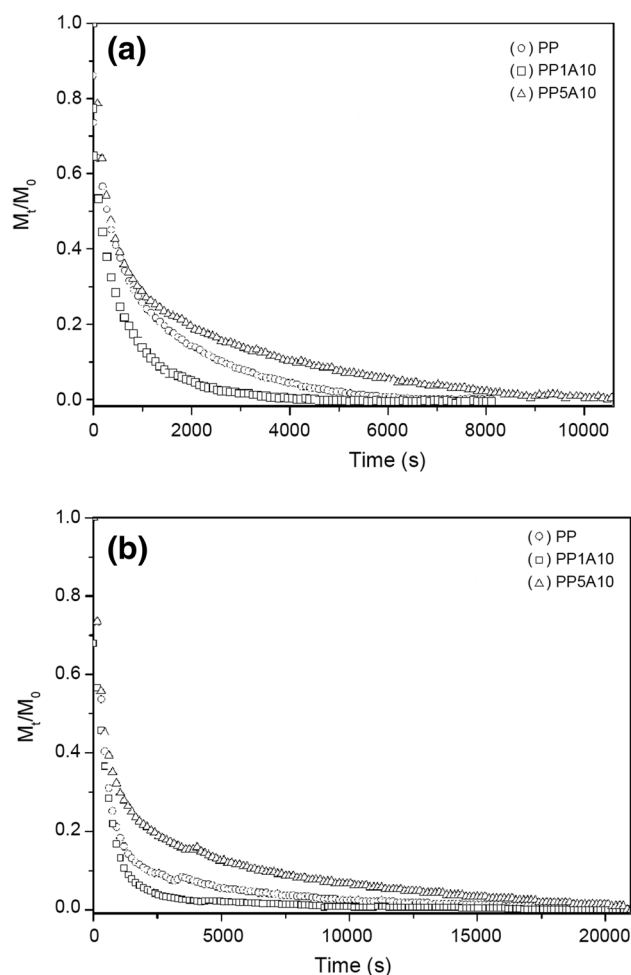
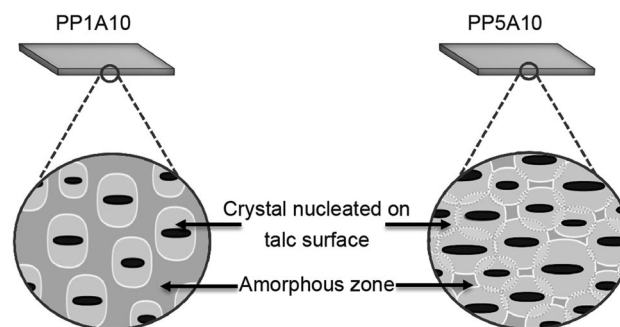


Fig. 3 Desorption curves of lemon essential oil for PP and nanocomposite films, obtained by: **a** gravimetry and **b** thermogravimetric analysis



Scheme 1 Representation of talc nanoparticles distribution and crystalline regions within blown nanocomposite film

links between adjacent chain-folded lamellae. These are the responsible that oil can interpenetrate among crystals nucleated on talc surface and it can be absorbed by the mineral particles. In the case of nanocomposite films with

low particle concentration (1 wt%) oil absorption by talc is negligible, which would explain partially the fast desorption in PP1A10.

Crystal orientation in the polymeric matrix also influences on the rate of oil desorption from nanocomposite films, being particularly evident for 1 wt% talc. This result is corroborated by the marked increase in $I_{(040)}/I_{(110)}$ ratio, as previously discussed for the analysis of XRD results (Table 3). This crystal orientation confines the amorphous regions within nanocomposite film, establishing preferential paths where the diffusion of oil molecules is not hindered. Moreover, low talc concentration (1 wt%) for PP1A10 leads to crystalline regions completely separated without any interconnection among them in film microstructure. Scheme 1 represents talc nanoparticle distribution and crystalline regions within blown film. Consequently, the penetrating molecules move faster through these amorphous delimited regions, reaching a high desorption rate compared to PP film.

Regarding to nanocomposite films with 5 wt% talc (PP5A10), a slower and prolonged desorption of essential oil is observed, compared to the other formulations (Fig. 3). This result can be explained in terms of oil molecules that must leave talc nanoparticles and then they must travel through the film, sorting the aforementioned obstacles in their diffusion path. As a consequence, a more slow and delayed release of essential oil molecules from nanocomposite films was observed.

Particularly, the influence of degree of crystallinity on lemon essential oil desorption can be avoided from the discussion related to the behavior of PP5A10 films. This fact is based on the negligible increment in the degree of crystallinity when 5 wt% talc was used in the nanocomposite films (Table 3). Moreover, crystal orientation does not affect the oil desorption due to the presence of 5 wt% talc which led to begin the extremities of adjacent crystals to impinge on one another, interfering with the orientation of crystalline regions. Thus, the mechanism of desorption for PP5A10 is mainly dominated by nanoparticle concentration and their distribution within the polymeric matrix. In this regard, particle concentration determines a spatial arrangement wherein the crystals nucleated at talc surface are interconnected among them, as it is shown in Scheme 1.

On the other hand, matrix swelling is strongly reduced and there is more oil absorbed by particles. All of these factors contribute to a slow oil desorption from nanocomposite films. In this sense, talc particles at 5 wt% showed the greater capability to retain the lemon essential oil along the time, demonstrating the purpose for which these mineral particles were used to retard the lemon essential oil release from nanocomposite films.

Conclusion

In this work, a systematic and detailed phenomenological analysis of essential oil desorption from PP/talc nanocomposite films was carried out. This is a complex system constituted by a semicrystalline polymer (PP) and talc nanoparticles, which are strong nucleating agents. Lemon essential oil was used as aroma model due to its notable swelling character. PP/talc films presented a homogenous particle dispersion, distribution and orientation within the polymer matrix. Besides, nanometric thickness of talc particles was corroborated by TEM for the two studied particle concentrations, ensuring the obtaining of nanocomposite formulations. In addition, a preferential orientation of polymer crystals in the (040) plane was determined by XRD, as a consequence of the blow extrusion process. Results from desorption of lemon essential oil obtained by two independent techniques (gravimetric and thermogravimetric analysis) showed that PP film has a desorption rate higher than nanocomposites containing 5 wt%, but lower than those with 1 wt%. This behavior is a consequence of the global crystallinity configuration changes produced by the nanoparticle concentration and the film obtaining process. Several factors such as swelling, tortuosity, crystals orientation, and talc oil absorption showed greater or less relevance dependence on talc concentration. For PP films, crystal orientation induced by blow extrusion process is the main obstacle for desorption mechanism. When 1 wt% particle was present in nanocomposite, oil release was mainly dominated by the diffusion through the preferential paths given by amorphous phases among crystals growing from nanoparticles. Besides, in this case, oil absorption by talc is negligible. Meanwhile, in nanocomposites containing 5 wt%, matrix swelling is reduced and there is more oil absorbed by particles. Furthermore, the presence of the particles and interconnected crystals entities increase the tortuosity, delaying the oil release. The present study evidences that consideration of tortuosity as unique factor to modify the diffusion mechanism in complex systems such as PP/talc nanocomposite films led to wrong conclusions. Then, an additional insight related to the desorption phenomenon of a strongly swelling oil in nanocomposite films, based on semicrystalline polymer and nucleating mineral particles was given, as well.

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