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PBAT/organoclay composite films—part 2: effect of UV aging on permeability, mechanical properties and biodegradation

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Abstract Biodegradable alternatives are required in order to minimize the environmental impacts caused by inadequate disposal of plastics, especially fast-discharge plastics such as those used in the packaging. This work studied the permeability, mechanical properties and biodegradability of PBAT/organoclay composite films. The materials were melt-mixed in an internal laboratory mixer, and films containing 1, 3 and 5% of organoclay were prepared in a chill roll extruder. The samples were subjected to UV radiation, and their properties were evaluated before and after accelerated aging. Results show that tensile properties, gas permeability and biodegradation depend on filler content and that oxygen and carbon dioxide permeabilities were affected by UV aging. Although the mechanical properties are negatively affected by filler incorporation, oxygen and carbon dioxide permeabilities decreased and biodegradability increased in the composites, making them an interesting option for use in packaging.

Keywords PBAT · Organoclay · Films · Biodegradability · UV aging

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Introduction

Plastic-made products are the focus of many debates and discussions related to environmental issues. Over the years, the inappropriate disposal of these products in the environment has led to serious environmental problems. Several researchers have looked for ways to minimize the negative effects of polymer disposal in the environment, and the use of biodegradable polymers is one of the alternatives to reach this goal as these polymers lead to sustainable products [1–3].

Composites and nanocomposites are an option for the use of biodegradable polymers, since biodegradable polymers are still fairly expensive. Filler addition to high-cost biodegradable matrices reduces the cost of the final product and may lead to products with improved physical and mechanical properties. Environmental and economic concerns are the reason polymer composites and nanocomposites based on layered silicates continue to attract widespread attention. Nanocomposites at low loading levels ($<10\%$ and usually $<5\%$) result in lower processing costs, and fairly high mechanical properties and optical clarity products that may be of interest for packaging. Nanoclays, organically modified or not, can be used to obtain composites and nanocomposites with biodegradable polymers [4–7].

The most promising nanoscale fillers are layered silicate nanoclays such as montmorillonite and kaolinite. In food packaging, major emphasis is given on the development of high barrier properties against the diffusion of oxygen, carbon dioxide, flavor compounds and water vapor. Antimicrobial properties also are often desired, and studies have shown that nanoclays and organoclays either have these properties or may be used as metal oxide carriers to obtain nanocomposites films with antimicrobial activity [8–11].

Poly(butylene adipate-co-terephthalate) (PBAT) is widely used in the production of biodegradable films for packaging, particularly in the food packaging industry [7, 12, 13], and it is among the most promising commercially available biodegradable polymers that can be used to make composites. PBAT is a synthetic aliphatic–aromatic copolyester, which combines biodegradability, supplied by its aliphatic portion, and good mechanical properties, supplied by the aromatic portion of its polymer chain. It has high melt strength and flexibility, high elongation at break and good processability, ideal characteristics for flat film extrusion. PBAT has been used in the manufacture of agricultural films and laminated films for solid food packaging, garbage bags and casings for reforestation [14, 15]. It is susceptible to photodegradation due to the presence of aromatic rings and carbonyl groups that act as photosensitizers. The benzene rings can absorb UV photons, but are also capable of dissipating absorbed UV light by electronic relocation. Carbonyl groups can absorb UV light and initiate the generation of free radicals [16, 17].

Organophilic clays can be used to manufacture composites with biodegradable polymers. PBAT/organoclay composite films with improved mechanical properties, improved thermal stability and low nanoclay content have been developed in recent years [5, 18, 19].

Someya et al. [20] studied PBAT/montmorillonite (MMT) nanocomposite films, prepared by melt intercalation, and investigated its aerobic biodegradability in soil tests. It was observed that, when buried in the soil, the mass loss of the nanocomposites was higher than the neat polymer, indicating that film biodegradation increased with MMT addition. Chen et al. [21] evaluated the mechanical properties of PBAT/organophilic clay nanocomposites and concluded that modulus and tensile strength increased, while elongation at break decreased with filler incorporation. These authors attributed the improvements in mechanical properties to better matrix/clay interaction promoted by the surfactant present in the organoclay.

This contribution investigates barrier, mechanical and biodegradability characteristics of PBAT/organoclay composites with 1, 3 and 5% of C20A organoclay, before and after undergoing accelerated aging by UV radiation.

Experimental

Poly(butylene adipate-*co*-terephthalate) (PBAT), under commercial name Ecoflex®, grade F-C1200, purchased from BASF (Germany) was used as the matrix. The polymer has a density of 1.26 g/cm^3 at room temperature, with a melt flow rate of 3–5 dg/min (ISO 1133, 190 °C/2.16 kg), glass transition temperature of -30 °C and melting point between 110 and 115 °C according to the manufacturer.

Cloisite®20A organoclay purchased from Southern Clay Products (USA) was used as a filler. It is a layered silicate (montmorillonite) with cation exchange capacity of 0.95 meq/g, modified with quaternary ammonium salt with two long-chain (C16–C18) aliphatic residues. According to the manufacturer it has a basal interplanar distance of 2.42 nm and a density of 1.72 g/cm^3.

Samples with 1, 3 and 5% organoclay content (by weight) were prepared in a Haake Rheomix 3000 laboratory internal mixer operating at 160 °C, 60 rpm for 10 min, and used to prepare films in a bench-scale single-screw extruder operating at 180 °C and 45 rpm. Details on processing are in Part I of this paper [22].

The films were aged by UV exposure according to ASTM D5208 in a weathering chamber under controlled temperature (50 ± 3 °C) and subjected to continuous UV irradiation for 5, 10, 20 and 30 days; fluorescent lamps were used with emission in the UVA region at 340 nm and 0.89 W/m^2 irradiance.

Oxygen and carbon dioxide gas permeabilities were measured at 25 °C in a GPD-C Brugger instrument according to ASTM D1434 standard. Tensile tests were performed according to ASTM D882, using an EMIC DL500 universal testing machine with a 20 N load cell operating at 50 mm/min constant rate of extension at ambient temperature. Scanning electron microscopy images of fractured surfaces were obtained in a FEI Quanta 650 FEG equipment; the samples were cryogenically fractured in liquid nitrogen and gold sputtered to avoid charge accumulation.

Biodegradation was performed by burial in soil prepared with manually mixed organic fertilizer, earthworm humus and fertile soil. Biodegradation testing was conducted in an incubator operating at 30–35 °C with air and soil relative humidity kept at 80 and 60%, respectively. The samples were buried in the soil prepared as mentioned, and weighted weekly to determine sample mass loss as a function of time.

Results and discussion

Accelerated UV aging

Photographs of unexposed and UV exposed samples are shown in Fig. 1.

The originally white surfaces turned yellowish to brown after 30 days under UV exposure. The change in coloration occurred gradually with the time of radiation exposure to radiation. The surface texture of the samples became wrinkled with aging time, indicative of the occurrence of structural changes of the samples.

Permeability

Oxygen and carbon dioxide gas permeability tests results were measured at 25 °C for the neat PBAT and PBAT/organoclay films with 1, 3 and 5% C20A before and after accelerated aging and are graphically shown in Fig. 2 (Table S1 in Supplementary Information).

As expected, gas permeability decreased with the presence and concentration of organoclay in the samples. Inert fillers act as barriers increasing the tortuosity of the path necessary for the gas to permeate through the sample [23]. Our data also indicate that, for all samples investigated, oxygen and carbon dioxide permeabilities significantly increased with aging time. These results contrast with the ones relative to physical and UV aging on amorphous polymers which showed gas permeability to decrease and gas selectivity to increase with aging. According to the authors, this would be a consequence of cross-linking and/or increased crystallinity [23–25].

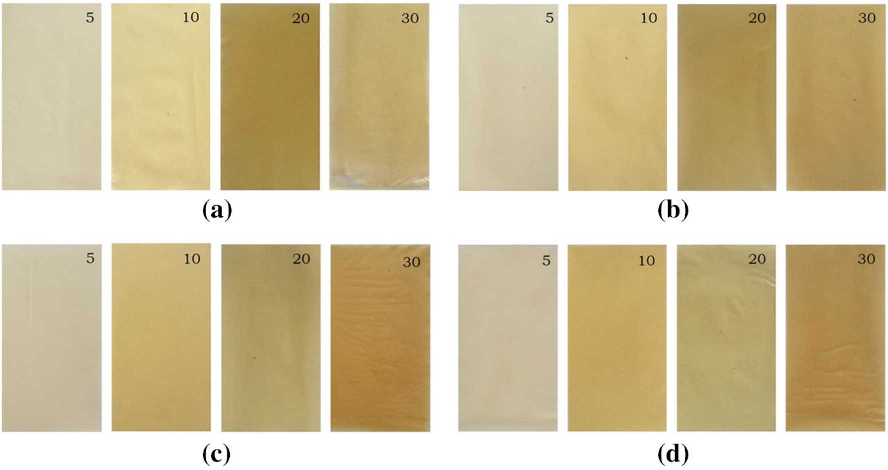


Fig. 1 Photographs of PBAT (**a**), PBAT/1%C20A (**b**), PBAT/3%C20A (**c**) and PBAT/5%C20A (**d**) test specimens illustrating samples yellowing under UV exposure. Exposing time (days) indicated

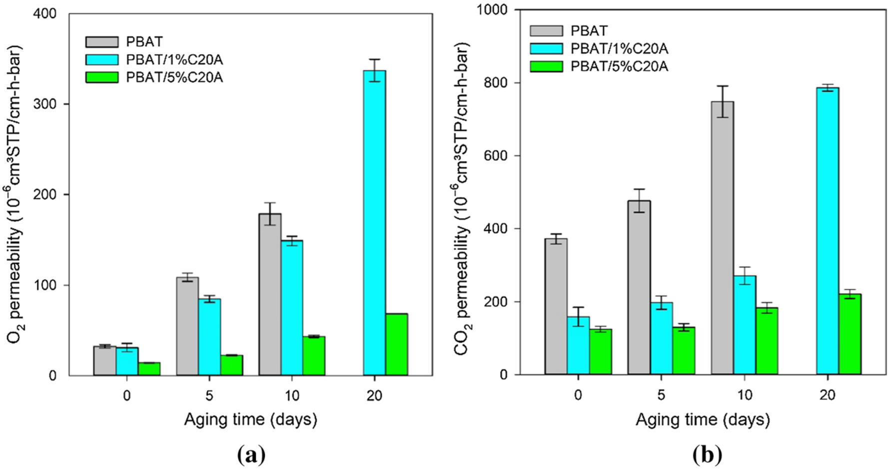


Fig. 2 Oxygen (**a**) and carbon dioxide (**b**) permeability at ambient temperature for PBAT and PBAT/organoclay nanocompound films before and after UV aging

It was not possible to determine the permeability of neat PBAT aged for 20 days because the samples became too porous (microscopic pinhole effect) or too fragile to properly seal under vacuum [26].

However, aging led to up to tenfold increases in oxygen permeability and up to fourfold in carbon dioxide permeability for the systems with 1% filler. Significant but more moderate increases in gas permeability as a function of aging time were observed for the sample containing 5% organoclay; in that case, up to 3.8-fold increase in oxygen permeability and up to 0.8-fold increase in carbon dioxide permeability were observed. It is believed that this increase results from microstructural changes of the matrix which also affects filler/matrix interaction. Gas permeation results seem to indicate that these interactions are decreased and/or that microscopic pinholes are formed.

Tensile properties

Tensile properties for PBAT and PBAT/organoclay compounds are shown in Table S2 and Figs. 3, 4 and 5 (Table S2 in Supplementary Information).

As expected, results indicate that tensile modulus of the composites was higher than that of the matrix and that it increases with filler addition and content, showing that stiffness was significantly affected upon compounding. Tensile strength and elongation at break decreased with the clay content, although this effect is less expressive for elongation. This indicates that this organoclay is not an active filler for PBAT or else filler/matrix adhesion is poor as addition of active mineral fillers to polymer matrices results in products with higher modulus and strength. UV aging significantly affected the tensile properties of PBAT and PBAT/C20A compounds. Tensile modulus increased with aging: 112% for PBAT and 167% for PBAT/3%C20A. Tensile strength decreased with increasing filler content and

Fig. 3 Effect of UV aging for indicated times on the tensile modulus of PBAT and PBAT/C20A composites

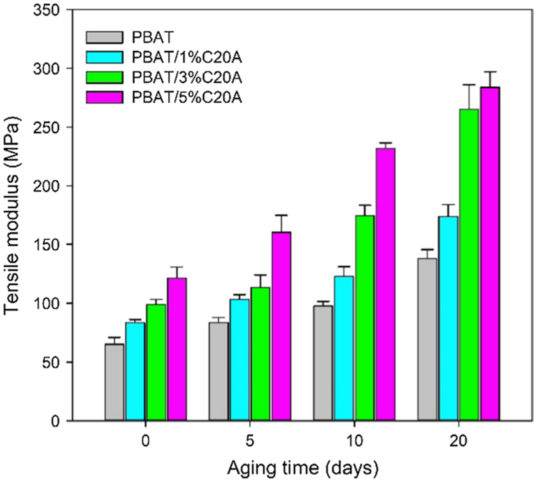
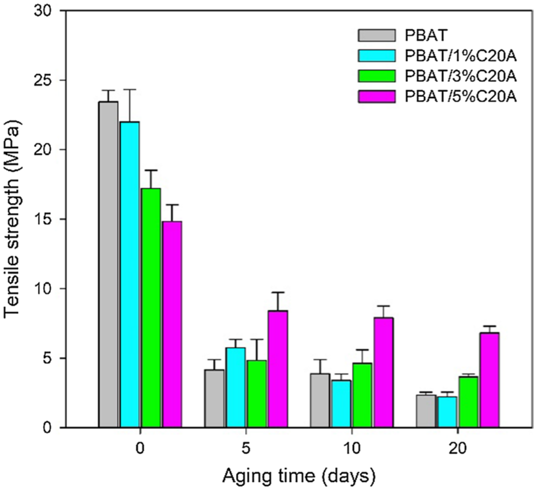


Fig. 4 Effect of UV aging for indicated times on the tensile strength of PBAT and PBAT/C20A composites



UV aging time. Decreases in tensile strength of about 6, 23 and 37%, respectively, were observed for pristine composites with 1, 3 and 5% organoclay, while reductions of up to 89, 79 and 54% for 1, 3 and 5% of C20A, respectively, were observed after 20 days of UV exposure. The effect of UV aging was catastrophic for all composites. These results suggest that filler incorporation into PBAT stiffened and weakened the PBAT and that these effects significantly increased with accelerated UV aging. It is likely that UV aging led to PBAT cross-linking [17], and perhaps even a slight change in crystallinity, but we believe crystallinity changes to be minimal and have little impact on tensile properties as PBAT is a copolymer of relatively low crystallinity copolymer (~ 15%) whose crystallinity did not change upon organoclay addition [22]. The decrease in mechanical

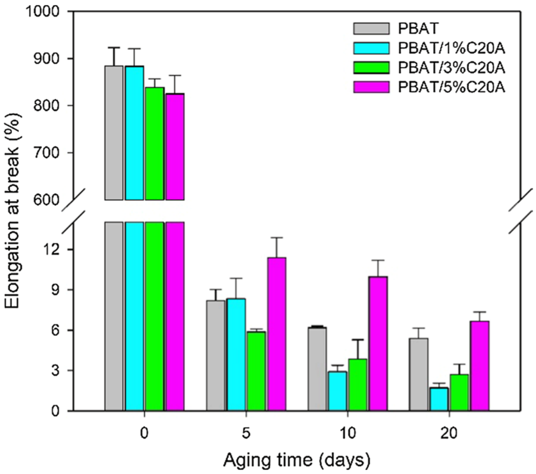


Fig. 5 Effect of UV aging for indicated times on the elongation at break of PBAT and PBAT/C20A composites

strength and increase in gas permeability with aging were most likely caused by poor adhesion which further deteriorated upon UV exposure.

Scanning electron microscopy (SEM)

SEM micrographs of PBAT and PBAT/organoclay composites acquired before and after accelerated aging by UV radiation for 30 days are shown in Figs. 6 and 7.

Phase separation between organoclay and polymer is not clearly observed. Before aging, a smooth and homogeneous surface is observed for PBAT, while that of the composites becomes more heterogeneous and rougher with increasing filler contents. Aging (Fig. 7) led to rougher and more brittle fracture surfaces in all systems. Additionally, organoclay agglomerates are observed in the composites. Similar morphology has been reported in another biodegradable polymer/organoclay system [27], and it is believed that filler aggregates and processing defects are responsible for the lower tensile strength and elongation at break values with increasing filler contents as observed in Figs. 3, 4 and 5.

Biodegradation

The results of mass loss for the soil biodegraded samples, before and after exposure to UV radiation, are shown in Fig. 8 (Table S3 in Supplementary Information).

Our data indicate that while PBAT degradation after 14 weeks being buried in soil is minimal (loses only 1% mass during this period of time), it degrades significantly 1 week after being exposed to UV radiation (49 and 62% after 5 and 30 days UV exposure). The total mass loss increases with exposure time for both the matrix and composites.

The degradation behavior of the nanocomposites differed from that of neat PBAT. Biodegradation kinetics of the irradiated nanocomposite samples was slower than

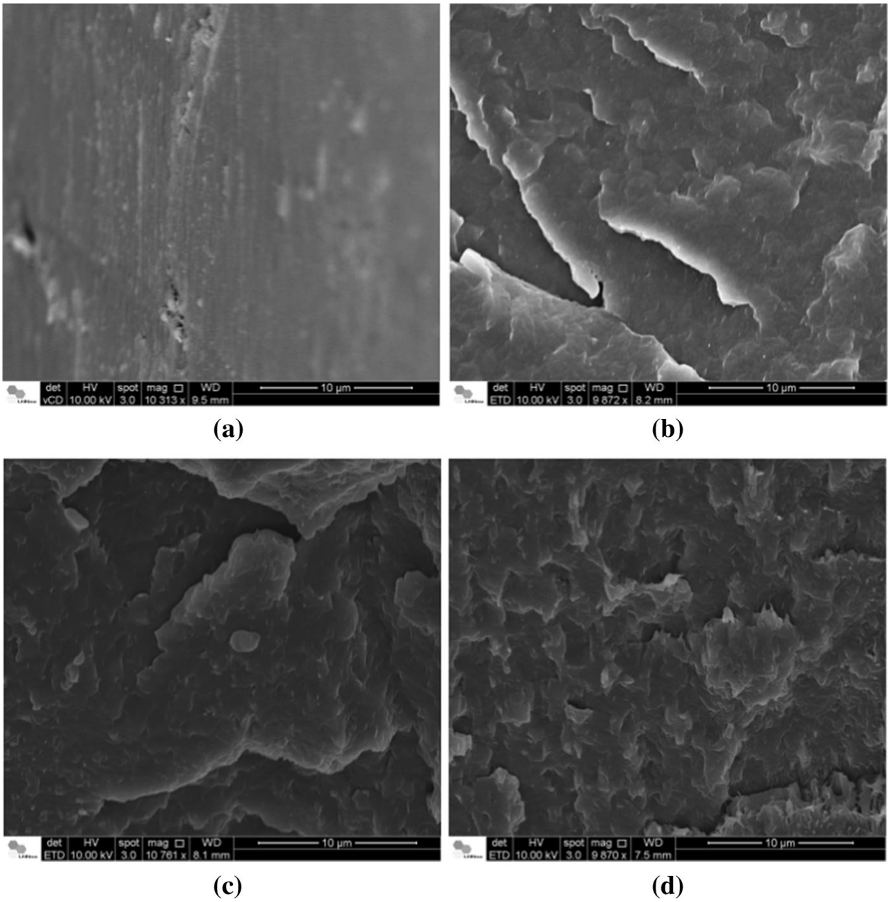


Fig. 6 SEM images of fractured surfaces of PBAT (**a**), PBAT/1%C20A (**b**), PBAT/3%C20A (**c**) and PBAT/5%C20A (**d**) before UV aging for 30 days. Magnification of 10,000×

that of the neat matrix, which can possibly be associated with PBAT cross-linking and organoclay antimicrobial activity [26, 28, 29].

For equal burying times of the irradiated samples, degradation of PBAT/1%C20A sample was more intense than that of PBAT/5%C20A composite: e.g., mass loss of 54% versus 26% after 7 weeks of soil burial, for 5-day-UV-aged samples with 1 and 5% of organoclay, respectively. However, the final weight loss at long times tended to increase with clay content and UV irradiation time, which can probably be associated with poor or decreased filler/matrix adhesion after irradiation leading to easier sample disintegration. This hypothesis seems to be confirmed by mechanical, permeability and SEM characterizations.

The results obtained indicate that, in order to undergo significant biodegradation (large loss of mass), PBAT must be pre-aged. Exposure to UV radiation and temperature may be necessary to break the bonds and change the chemical structure of

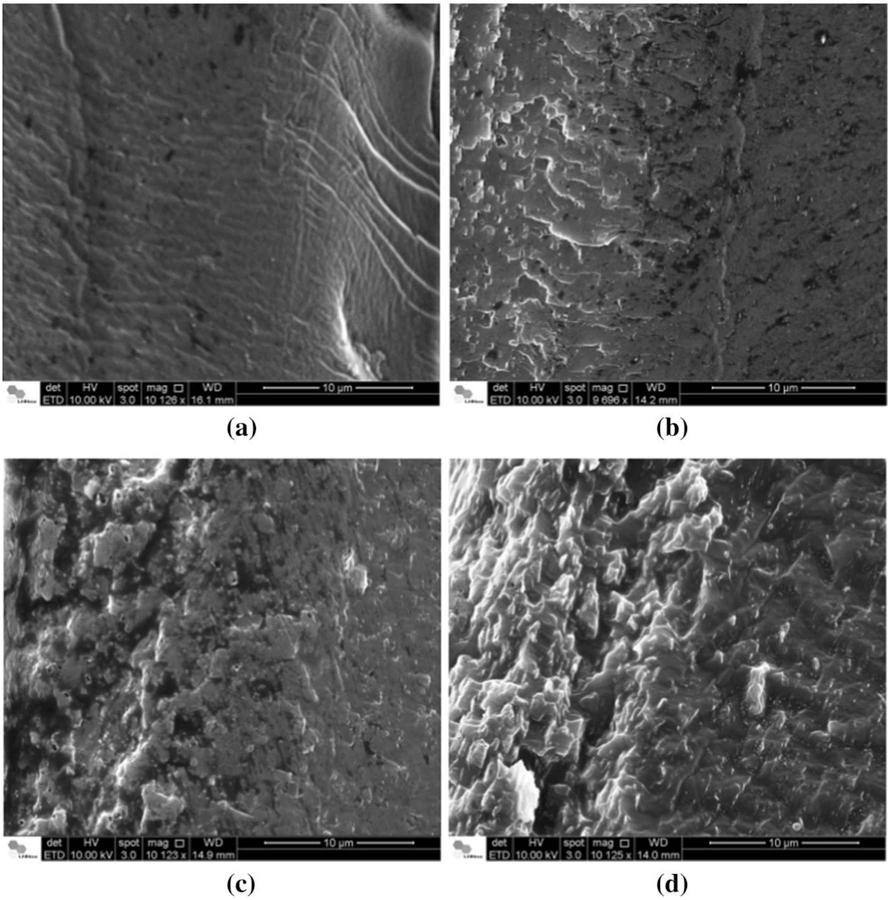
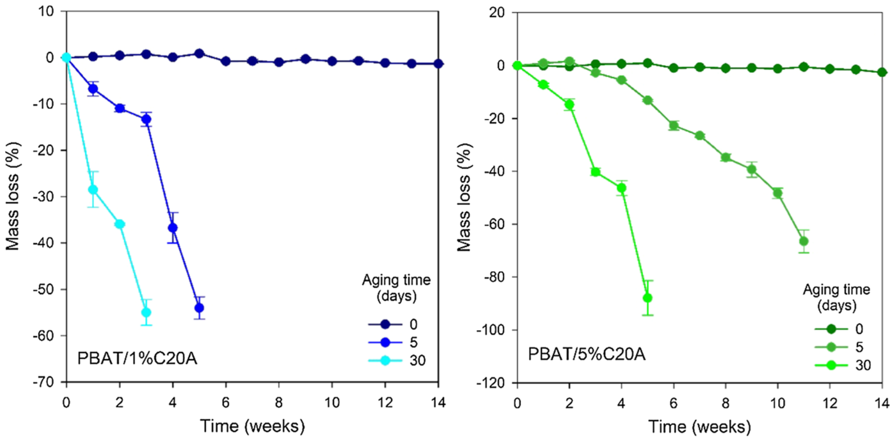


Fig. 7 SEM images of fractured surfaces of PBAT (**a**), PBAT/1%C20A (**b**), PBAT/3%C20A (**c**) and PBAT/5%C20A (**d**) after UV aging for 30 days. Magnification of 10,000×

PBAT, resulting in its fragmentation. In general, materials before being composted spend long periods exposed to the open sky absorbing various types of radiation and subjected to various climatic conditions, which may favor biodegradation.

Conclusions

Results indicate that aging by UV radiation increases while filler content decreases oxygen and carbon dioxide permeabilities of PBAT/organoclay films. The tensile strength is strongly affected by filler presence and content as well as by accelerated aging. PBAT/C20A composites biodegrade more than the neat PBAT. All these results show that compounding PBAT with up to 5% of organoclay is an alternative for the production of packaging films, since they combine matrix biodegradability



(a) (b)

Fig. 8 Effect of UV aging for indicated times on mass loss of PBAT/1%C20A (**a**) and PBAT/5%C20A (**b**)

with good barrier properties and reasonable mechanical behavior. PBAT/C20A films can be used in the packaging industry where discarding is fast. Discarded film biodegradability will be significantly accelerated by UV radiation, intensely present in the common places of disposal of these materials.

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