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RESEARCH ARTICLE

Multilayer Nanocomposite Polymetric Packaging For Microwave Applications

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ABSTRACT

Microwaveable packaging material should ensure good preservation of the product before cooking/ heating such as high barriers to gases and aromas and adequate control of water vapor transmission. Among the polymers used in flexible packaging, crystalline poly(ethylene terephthalate) (CPET) is characterized by good oxygen barrier properties and quite high heat stability which ensures the absence of alterations of foods flavors. CPET trays or films are suitable for Ready To Cook (RTC) products within a temperature range from -40 to + 220°C.

The aim of this work was the production and characterization of nanocomposite multilayer PET films, for microwave applications, in which the nanoclay acts as a heating enhancer. Films prototypes were made by means of laboratory compounding equipment for the production of nanocomposite CPET and by a co-extrusion equipment for producing multilayer films using two different PET copolymer matrices and a modified nanoclay (Cloisite 20A) as heating enhancer. The study of morphology of nanocomposite layer by means of X-ray diffraction experiments was carried out in order to correlate the intercalation/ exfoliation degree of nanoclay with cooking performance.

1.0 INTRODUCTION

Microwave (MW) heating has many applications in the field of food processing which include drying, pasteurization, sterilization, thawing, tempering, baking and preservation of food materials [1]. Microwave heating has gained popularity in food processing due to its ability to achieve high heating rates, significant reduction in cooking time, more uniform heating, safe handling, ease of operation and low maintenance [2, 3]. However, the main limits in microwave ovens usage are often related to the adequate choice of packaging materials suitable for such technology. Microwaveable packaging material should ensure good preservation of the product before cooking/heating such as high barriers to gases and aromas and adequate control of water vapor transmission [4]. Moreover, it must be transparent to microwaves, thermally stable and resistant to the mechanical stress induced by volatile substances in the head space during cooking process. In the last years, a great interest is devoted to find innovative solution based on flexible packaging and the use of additives or systems that act as susceptors or heating enhancers for improving the characteristics of polymers in cooking/heating in MW ovens.

The advantage of using flexible packaging is related to the ability to contain food with irregular shape and to maximize the contact between food and the part of packaging containing susceptor or heating enhancer materials [5]. Susceptors are substances that, once located in the packaging, allow to reach high local temperatures during MW heating, imparting the properties of crunchiness and browning, typical of a product heated in a conventional oven, to the food [6, 7]. Heating enhancers or cooking optimizers are, instead, systems uniformly distributed in the packaging structure that act reducing the cooking times and standardizing the heating time of the product [8, 9].

Among the polymers used in flexible packaging, crystalline poly(ethylene terephthalate) (CPET) is characterized by good oxygen barrier properties and quite high heat stability which ensures the absence of alterations of foods flavors.

CPET trays or films may be intended for Ready To Cook (RTC) products both for microwave and for traditional ovens, as the product can be used within a temperature range from -40 to + 220°C. Moreover, the wide range of operating temperature satisfies the needs of consumers for containers with a good impact resistance at low temperature and stability at high temperatures.

The aim of this work was the production and characterization of nanocomposite multilayer PET films, for microwave applications, in which the nanoclay acts as a heating enhancer.

Films prototypes were made by means of laboratory compounding equipment for the production of nanocomposite CPET and by a co-extrusion equipment for producing multilayer films using two different PET copolymer matrices and a modified nanoclay (Cloisite 20A) as heating enhancer.

The study of morphology of nanocomposite layer by means of X-ray diffraction experiments was carried out in order to correlate the intercalation/exfoliation degree of nanoclay with cooking performance.

2.0 EXPERIMENTAL

2.1 Materials

To produce nanocomposite films were used two aromatic copolyester matrices:

- PET Cleartuf ULTRA New Add (Ultra NA), supplied by M&G Polimeri Italia, copolyester bottle grade, blended with an experimental patented additive based on titanium oxide and with an intrinsic viscosity of 0.80 ± 0.02 dl/g.

- Poly(ethylene terephthalate) (PET) Cleartuf ULTRA Standard (Ultra STD), copolyester containing carbon black with an intrinsic viscosity value of 0.82 ± 0.02 dl/g, supplied by M&G Polimeri Italia;

The nanofiller used for this study was:

- Cloisite 20A (C20A), provided by Southern Clay Products, a modified montmorillonite with dimethyl - dihydrogenated tallow - quaternary ammonium salt. The cation exchange capacity of the silicate is about 95meq/100g and the surfactant content is about 38% (wt/wt). Previous studies permitted to identify this silicate as good candidate to obtain a good intercalation degree with PET matrices [10].

2.2 Films Production

PET nanocomposite films production was made with two different extrusions. In the first step nanocomposite materials were produced by melt compounding using a twin screw extruder Collin ZK25, equipped with two co-rotating intermeshing screws with a ratio L/D=42. A gravimetric feeding was set to obtain nanocomposite pellets containing respectively 0wt% 2wt% and 4wt% of C20A into the matrix. The temperature profile used in the melt compounding process is reported in Table 1.

T8=TDIE	T7	T6	T5	T4	T3	T2	T1
205	280	280	280	280	276	260	250

Table 1. Temperature profile (°C) used during melt compounding process.

Nanocomposite materials were obtained extruding at a screws speed rotation of 100 rpm. The resulting materials were cooled in a water bath and pelletized for using in film production step.

Multilayer films were produced using a pilot scale co-extrusion equipment consisting of two single screw extruders Collin Teach-Line E20T, connected to a feed block system linked to a coat-hanger type head, and then by chill-rolls system. The equipment was set to obtain a symmetrical three-layer film structures "ABA" type. The thickness ratio of the three layers was maintained constant at percentages of 10/80/10 and the films thickness were approximately 35 μm. The extruder A was set at 280°C, while the extruder B was set at 275°C. The feed block and the die were set respectively at 275°C and 280°C. Different compositions of the core layers as reported in Table 2. External layers were made of neat matrix of the same type of the core layer which contains the nanocomposite system. Before any processing step, materials were dried under vacuum at 120°C for 18 hours in order to prevent hydrolysis phenomena induced by moisture.

2.3 Methods

Morphological study of produced films and intercalation degree of nanocomposite materials were analysed by means of X-ray diffractometry tests using a diffractometer D8Advance (Bruker) Ni filtered with a CuKα radiation λ=1.5406 Å, 35 kV, 40 mA. Scans were recorded at a scanning rate of 0.6 deg/min in the range 2θ = 2–40°.

Microwave experiments were carried out using a conventional microwave oven (DeLonghi MW401) on pork meat hamburgers of about 30g, with a diameter of 5cm and a thickness of 1cm. Meat samples were packaged in pouches of 15x12cm^2, obtained by heat-sealing. MW heating treatments were performed for a fixed time of 60 seconds, measuring hamburger core temperature by a suitable thermocouple (FISO Technologies Inc.). Tests were carried out at two different powers: 550W (Method P1) and 750W (Method P2). Temperature trends of the sample core were recorded for each sample. Preliminary tests were conducted using a commercial CPET (crystalline PET) film for

Film Sample	External Layers "A"	Core Layer "B"
MULTI NA	Ultra NA	Ultra NA
MULTI NA 2%	Ultra NA	Ultra NA - C20A 2 wt%
MULTI NA 4%	Ultra NA	Ultra NA - C20A 4 wt%
MULTI STD	Ultra STD	Ultra STD
MULTI STD 2%	Ultra STD	Ultra STD 2 wt%
MULTI STD 4%	Ultra STD	Ultra STD4 wt%

Table 2. Co-extruded multilayer films structure.

Film Sample	2θ [°]	d001 [nm]
C20A	3.84	2.30
MULTI NA 2%	2.84	3.11
MULTI NA 4%	2.87	3.08
MULTI STD 2%	2.89	3.06
MULTI STD 4%	2.87	3.08

Table 3. 2θ and d-spacing for C20A and three-layer nanocomposite films.

microwave application, to evaluate the efficacy of nanoclays as heating enhancers.

3.0 RESULTS AND DISCUSSION

3.1 X-Ray Diffraction Tests

Nanocomposite films were subjected to morphological characterization analysis by X-ray diffraction analyses. Results are reported in Table 3. C20A shows two peaks: the first one at 2θ= 3.84° corresponds to a interlamellar distance $d_{(001)}$ of 2.30 nm and represents the reference peak for the evaluation of the exfoliation/intercalation of the nanocomposite systems.

Multilayer films produced with Ultra NA matrix at 2wt% and 4wt% of nanoclay content, show a definite peak for 2θ angles respectively of 2.84° and 2.87°, at the diffraction plain $d_{(001)}$. Such behavior, already observed and reported in the literature, corresponds to a disordered intercalation [10]. Films of nanocomposite MULTI STD with 2wt% and 4wt% of C20A, show a definite peak for 2θ angles respectively of 2.89° and 2.87° corresponding to the plain diffraction $d_{(001)}$.

It could be observed an increase of the interlamellar distance which is clearly related to the intercalation of the system.

3.2 Cooking Tests

To evaluate the effectiveness of produced multilayer films in reducing heating time of a food sample, cooking tests of 60 seconds at a power of 550W (P1) were carried out using a microwave oven monitoring the core temperature of samples.

Preliminary tests were performed to compare the behaviour of CPET films and samples based on MULTI NA and MULTI STD. Results, shown

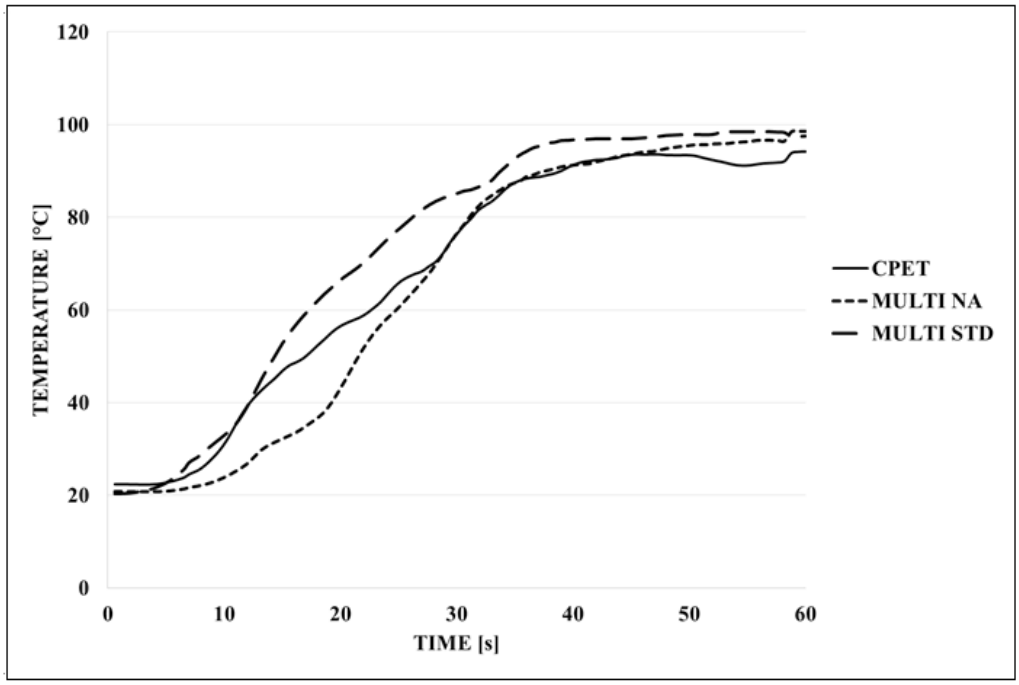

Fig. 1. Comparison between microwave cooking performances on pork meat packed with commercial CPET and prototypal multilayer films with method P1.

in Figure 1 as temperature increasing versus time, exhibit that the meat samples packaged in MULTI NA and MULTI STD films reached a higher maximum temperature than CPET samples. In particular, meat samples in MULTI STD reached the highest temperatures in a shorter time.

In Figure 2 are shown cooking tests results conducted with a power of 550W (Method P1) of nanocomposite prototype films. It can be observed that MULTI NA 4% (Figure 2a) and MULTI STD 2% (Figure 2b) samples show a faster increase of cooking temperature than MULTI NA 2% and MULTI STD 4%. These results are related to morphological results, which showed a less dispersion of the nanofiller in the samples with better cooking tests results. In addition, preliminary tests conducted using a power level of 750W (Method P2), show that both nanocomposite systems have a better behavior than samples of pure matrix only, with higher temperatures reached (up to 5°C higher) and reduction in cooking times (approximately 10 seconds less).

4.0 CONCLUSIONS

The aim of this work was the production and characterization of new multilayer nanocomposite polymeric packaging for microwave applications. The selected matrices were two different type of Poly(ethylene terephthalate): Ultra NA (modified with titanium oxide) and Ultra STD (modified with carbon black). Nanocomposite co-extruded multilayer films were produced using different percentages (2 and 4%wt/wt) of Cloisite 20A (C20A). The C20A was used as heating enhancer of PET, for reducing the heating time of food in a conventional microwave oven. Films were analysed for

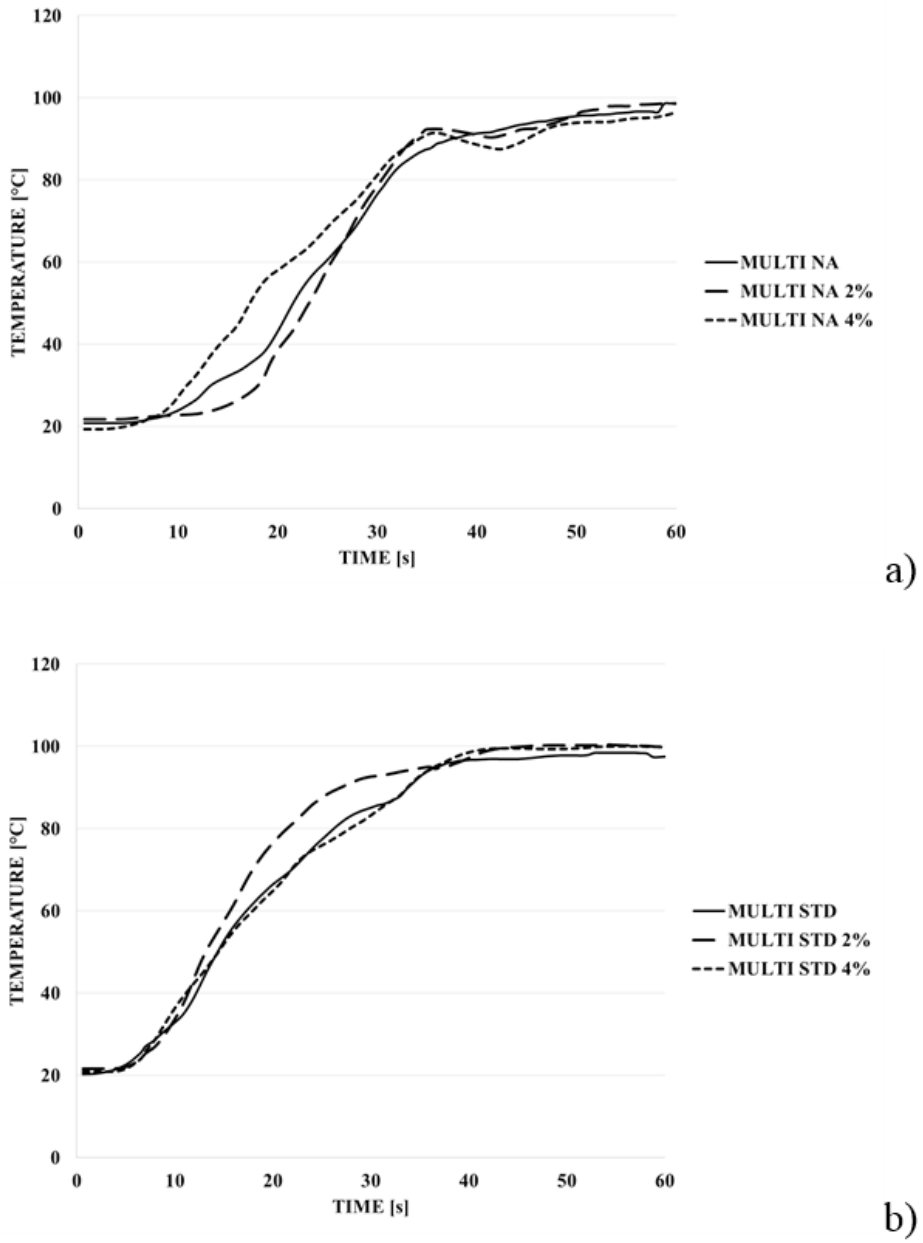

Fig. 2. Temperature profiles of pork meat hamburgers packaged in prototype films during microwave cooking tests with Method P1.

evaluating the effect of nanofiller on the prototypes morphology. In order to verify the effectiveness of the designed systems in reducing the cooking times of meat products, MW heating tests were carried out on meat samples in MW oven at two supplied powers. The cooking tests have pointed out that the selected matrices are efficient in reducing cooking times, if compared with a commercial CPET for microwave uses. Furthermore, low concentration of C20A acts as heating enhancers of PET. In particular, each nanocomposite sample had better performances than neat matrix films. Better results came out from MULTI NA 4% and MULTI STD 2% films, with Method P1, that show faster increase in cooking temperature. These results allow focusing the attention on the relation between morphological and cooking tests results. In fact, it can be observed that samples with better cooking tests results show a less dispersion of the nanofiller. This behavior might suggest that no high intercalation or exfoliation are necessary to have heating enhancer behavior of Cloisite 20A.

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