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MICROBIAL SAFETY OF PLASTIC MATERIALS OBTAINED FROM WASTES

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Abstract

Extensive use of plastics leads to the increase of non biodegradable wastes that have to be recycled due to both dramatically decrease of natural resources to producing them and to their increasing need as well as due to environmental issues. Most of goods made by materials based on wastes have to be commonly used by people. Antibacterial character of those is necessary to avoid epidemics. This paper deals with determination of antimicrobial character of materials based on polymeric wastes in comparison with virgin polyolefins. Surface contamination, total number of germs, *E. coli* and *Enterococci* growth on the samples surface have been determined and correlated with the surface characteristics of materials (hydrophobicity, surface energy, polarity, charge, roughness) as well as with bulk characteristics such as Young Modulus, crystallinity, water sorption. The conclusion of this study is that materials based on wastes are more sanitary safe by comparing to virgin polymers obtained without antimicrobial additives. This is due to possible maintaining in wastes of active antibacterial additives used in the plastic goods processing. High crystallinity and low water sorption avoid their release. Surface conformation seems to not fit to bacteria shape and dimensions, hindering their adhesion and growth. Negatively charged surface repels negative bacteria. Lower surface hydrophily of wastes, coming from OH and CO groups' elimination, due to photo-degradation during their life cycle, determines lower adhesion of more hydrophilic bacteria such as *E. coli*.

Key words: antibacterial character, polymeric wastes, polyolefins, roughness, stiffness

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1. Introduction

Extensive use of plastics in all areas of human activity leads to the accumulation of huge amounts of waste, mostly non-biodegradable. This creates major environmental problems by polluting soil, water and atmosphere due to their uncontrolled degradation and emission of toxic compounds.

Plastics recycling has became a necessity. Before the decision of incineration or recycling through pyrolysis or gasification, mechanical recycling of plastics can introduce plastics to a new life cycle for consumer goods with the minimum energy consumption (Corăbieru et al., 2014). Plastic waste will be collected and separated as secondary raw materials that can replace partially or totally virgin polymers in obtaining products made of plastics (Achilias et al., 2007; Al-Salem et al., 2009; Ashori and Nourbakhsh, 2009; Goodship, 2007; Hamad et al., 2013). But their use is still at a low level because of both objective and subjective reasons.

Objective reasons are related to continuous collection and separation possibilities of waste and in sufficient amounts to provide the rhythmic need of raw materials for industrial production. Also the

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effectiveness of separation methods must ensure reproducible quality of plastics separated. Contaminants can decisively influence the quality of final products.

A number of variables in plastic waste such as color, type of additives used, form of the polymer (film, foam, compact) will influence both the separation process and the properties of the material derived from these secondary raw materials. Also very important are the prejudices and psychological thresholds related to acceptance in everyday use of waste as secondary raw materials. Thus, fear of damaging the facilities for obtaining plastic products (extruder, injector, moulds, etc.) with pieces of metal, glass or ceramic, accidentally not separated, fear of inability to guarantee the final properties of the product due to the use of waste with variables and uncontrollable properties, fear of a narrow market of products made from recycled materials as black color, accepted for this kind of products in order to avoid uncontrolled variation in the final product color, is less attractive and limits their design. Finally yet importantly, given that the concept of waste (especially the household) is mentally linked to the notion of dirt, infection, decay, bacteria, microbes, their use is drastically limited.

Exponential growth of the population and decreasing oil supply (the raw material of synthetic polymers) are two key reasons for the development and acceptance of goods from recycled plastics for use in common areas of activity. The need for common use of spaces and objects require antimicrobial nature of materials that lead to the production of floors, panels, furniture, toys etc. so they do not become vectors to transmit pathogens, causing epidemics (Lagaron et al., 2012).

In this paper we intend to test whether plastic waste materials separated from the municipal solid waste (MSW) favor the development of surface pathogenic bacteria, to a larger extent than materials obtained from virgin polymer. The answer to this question is very important both for the public acceptance of using recycled plastic products and broadening their appliance.

Also the surface microbiology correlation with other features such as roughness, surface energy, water adsorption capacity from the atmosphere or at immersion and with material characteristics such as composition, crystallinity and rigidity will allow deeper knowledge about the behavior of different fractions of polymeric waste. In spite of similar extensive studies applied on biomaterials (Marciano et al., 2009; Sivakumar et al., 2010), to the best of our knowledge, these issues have not been addressed in the literature to the plastics obtained from wastes.

2. Materials and methods

2.1. Raw materials

Three types of virgin polyolefins [POs] have been used: polypropylene [PP] homopolymer (trade name Moplen HP400R provided by Basel Polyolefins; MFR 25 g/10 min – at 230°C and 2.16 kg, ρ = 900 kg/m^3), high density polyethylene [HDPE] (trade name HDPE B5823 provided by Sabic; MFR 0.16 g/10 min – at 190°C and 2.16 kg, ρ = 958 kg/m^3), and low density polyethylene [LDPE] (trade name Lupolen 3010 D purchased from Lyondell Basel Industries; MFR 0.25 g/10 min – at 190°C and 2.16 kg; ρ = 927 kg/m^3).

Plastic wastes used in this study were collected and selected from Municipal Solid Wastes [MSW] by specialized Urban Enterprise from Brasov, Romania, in September 2010, in the frame of the European Project FP7 W2-Platics. 50 kg of polymeric wastes coming from the real wastes flux have been used as stock for different studies aiming to improve the separation process and to find more efficient ways for polyolefins recycling.

2.2. Obtaining material for testing

The waste polymer derived from MSW was washed, frozen and ground, obtaining particles with the size of 2-3 mm. It has been tested as such (coded MW 1-13), or separated through water flotation method.

In the frame of this study, a light fraction (coded: MW 3-6, with a density between: 0.884 and 0.964 g/cm^3) and a heavy fraction (coded: MW 7-13 with a density greater than 0.964 g/cm^3) have been also used for further studies.

Both pure polymers and the three samples obtained from waste were subsequently frozen and ground in a ZM 2000 centrifugal mill to obtain a homogeneous mixture (0.5-1 mm particles). Then pure polymers were melting mixed in a Brabender extruder at temperatures of 130, 140 or 175°C depending on the nature of the polymers used, at a mixing speed of 60 rpm for 10 minutes.

Time of mixing has been chosen at 10 minutes and it was kept constant in all the experiments, aiming to ensure a good homogenization of the melt material, proved in case of wastes, which particles have different colors, by the uniformity of the sheet color. For samples obtained from wastes, higher temperatures have been used for melt mixing, because of the complex composition of fractions: 180°C for fractions having higher content of polyolefins and 220°C for fraction with higher content of contaminants. The resulting mixture was then pre-melted for 10 minutes, and pressed in a Carver press at 140, 150 or 180°C for 6 minutes, obtaining sheets of 150x150x1mm (LxWxH).

In all samples only Irganox 1076 (0.5%) has been used as antioxidant.

2.3. Materials characterization

2.3.1. Determination of plastic waste composition

MSW plastic waste was separated in order to be characterized, through flotation method in 13 fractions of density using water (ρ = 0.997 g/cm^3) and solutions with different densities: ethylic alcohol: water (ρ = 0.788 g/cm^3, 0.880 g/cm^3 0.908 g/cm^3, 0.923 g/cm^3, 0.935 g/cm^3, 0.964 g/cm^3) and aqueous salts solutions of NaCl and Na_2CO_3 (ρ = 1.0053 g/cm^3, 1.1029 g/cm^3, 1.1469 g/cm^3; 1.197 g/cm^3, 1.27 g/cm^3).

Composition of the MW1-13 waste and of each fraction obtained by separation was determined by combining the gravimetric method with the interpretation of images using Photoshop CS5 software and FTIR-ATR spectroscopy, as described in a previous paper (Patachia et al., 2011). For spectral analysis it was used a Perkin Elmer type BXII spectrometer with ATR device. Scanning range is between 600 and 4000 cm^{-1} at a resolution of 2 cm^{-1}, the spectra recorded represents the average of four successive scans. Spectra obtained were processed through software device. To identify the components of the waste, Essential FTIR database was used.

2.3.2. Determination of thermal processed material's composition

Materials, resulted after mixing in the melt, were analyzed by ATR FTIR spectroscopy to test whether thermal degradation phenomena occurred after processing of polymers. The obtained spectra made possible the calculation of hydroxyl index (HI) and carbonyl index (CI) as the ratio of characteristic bands area (Eqs. 1 and 2) (Moldovan et al., 2013):

$$CI=A_{(1850\text{-}1650)} / A_{PO} \qquad (1)$$

$$HI=A_{(3600\text{-}3000)} / A_{PO} \qquad (2)$$

where:

- A_{PO} represents the reference area of POs, that presents maximum of absorption in the region of 2700-3000 cm^{-1} both for PE and for PP;
- $A_{(1850\text{-}1650)}$ represents the area of the carbonyl band (with the maximum of absorption at 1715 cm^{-1}) (Longxiang et al., 2005);
- $A_{(3600\text{-}3000)}$ represents the area of the hydroxyl band.

2.3.3. Mechanical analysis of materials obtained from virgin and waste polymers

Bone-shaped specimens according to EN ISO 527-1 STAS were mechanically tested using a Zwick Z020 mechanical testing machine, 10 mm/min, according to SR EN ISO 527-12/1996 determining the tensile strength, Young's modulus and relative elongation.

2.3.4. Determination of material crystallinity

To monitor changes in the crystallinity of the samples two methods were used:

- DSC method by which the crystallinity index was calculated by dividing the melting enthalpy of the mixture to the enthalpy of the 100% crystalline polymer as given by Eq. (3) (Crompton, 2006):

$$\chi_{DSC} = \sum_{i=1}^{n} \frac{\Delta H_{mi}}{\Delta H_{mi}^{0}} . a_i \qquad (3)$$

where:

- ΔH_{mi} is the melting enthalpy of i component from the mixture,
- ΔH_{mi}^{0} is the melting enthalpy of i component 100 % crystalline,
- a_i is the percent in which the polymeric i component is present in the mixture.

All measurements were performed using equipment from Perkin Elmer Diamond DSC in an inert atmosphere (N_2) from 0ºC to 300ºC with a heating rate of 10°C/min, 10-15 mg of the sample were closed in an aluminum capsule. In all cases there were two heating cycles, the first cycle aimed at removing the influence of heat treatments on materials and consequently on their properties. X-ray diffraction (Bruker-AXSD8 Advance Cukα1, λ = 154016Å, $2\theta = 10 \div 60^0$) by which both absolute crystallinity of the material analyzed and the presence of other crystalline substances (additives) was determined.

All the significant 2θ crystalline peaks have been taken into account according to Eq. (4):

$$\chi_{XRD} = \frac{\sum A_c}{\sum A_c + \sum A_a} \qquad (4)$$

where:

- χ_{XRD} - is the total crystallinity of the sample,
- A_c – crystalline peak area,
- A_a – amorphous peak area.

2.3.5. Determination of contact angle

Measurements were made with type SCA20 goniometer (Data Physics Instruments), and its software. The software enables the calculation of the contact angle formed between the tangent to the circle that describes the outline of the droplet and the surface of the material to be analyzed, thereby determining the wetting ability of the liquid used in the analysis. Test liquids used were water, glycerin and 1-Br-naphthalene. Values of surface tension and polar and dispersive components are found in the literature (Mohammed-Ziegler et al., 2004). Measurements were performed in at least five different points, for each fluid, and the average value was reported.

During the tests, the volume of the droplet was kept constant at 10 µl, and the contact angle was recorded immediately after the droplet felt on the analyzed surface. Also the surface free energy of materials obtained was determined, based on the relationship developed by Owens, Wendt, Rabel and Kaelble (Eq. 5), which took into account dispersive (d) and polar (p) components (Eq. 6) of the surface tension γ (Castell et al., 2004; Erbill, 2007).

$$\gamma_{SL} = \gamma_{SV} + \gamma_{LV} - 2\left(\sqrt{\gamma_{SV}^{d}\gamma_{LV}^{d}} + \sqrt{\gamma_{SV}^{p}\gamma_{LV}^{p}}\right) \quad (5)$$

$$\gamma_i = \gamma_i^d + \gamma_i^p \quad (6)$$

In Eqs. (5, 6) the symbols and notations have the following meanings:

γ_i is the surface tension at the interface liquid-solid (solid/vapors or liquid/vapors). It has two components: γ_i^d representing dispersive component of the surface tension and γ_i^p that represents the polar component of the surface tension.

Due to the influence of the surface electric charge on the bacteria adhesion and colonizing, the surface energy of the samples has been calculated also by using the Lifshitz-van der Waals and Lewis Acid-Base (LW/AB) approach, with the help of the instrument's software. According to this approach, the surface energy (γ) is decomposed into a Lifshitz-van der Waals (γ^{LW}) dispersive component as well as into a polar component - γ^p - with Lewis acid (γ^{p+}) and Lewis base (γ^{p-}) contributions respectively (Eq. 7) (Rudawska and Zajchowski, 2007).

$$\gamma = \gamma^{LW} + \gamma^{p} = \gamma^{LW} + 2\sqrt{\gamma^{p+} \cdot \gamma^{p-}} \quad (7)$$

The initial contact angle θ_0, which is the contact angle at the beginning of wetting process (for $t = 0$) for the test liquids was used in the calculation of surface energy.

2.3.6. Determination of roughness by Atomic Force Microscopy

Surface morphology was studied in semi-contact mode using atomic force microscope Scanning Probe Microscope Solver PRO-M, NTMDT, with scan sensor cantilever type NSG 10-Au (features: 3.4 X1, 6x0, 3 mm cuboidal body sensor tip (L) 95 x (W) 30 x (T) 2 mm, with 240 kHz resonance frequency and force constant 11.8 N/m). The analysis was conducted under laboratory conditions 25°C air temperature, and the images obtained were processed using the software on the device, aiming to determine the roughness of studied surface.

2.3.7. Qualitative determination of water vapors adsorption from the atmosphere

Qualitative assessment of adsorption of water vapors from the atmosphere on analyzed samples was performed by determining the difference between the absorption bands areas of OH groups (3400 cm^{-1}) from FTIR spectra corresponding to samples conditioned in laboratory atmosphere and those conditioned in a $CaCl_2$ desiccator.

2.3.8. Determination of adsorption of water at samples immersion

Of each type of composite, cylindrical samples (dxh: 10x1 mm) were cut using a perforating punch. These samples were conditioned in an oven at 80°C for 24 hours and then were weighed (m), considering the sample at time t_0 (all calculations of adsorption of water will relate to this value). Each sample was immersed in 20 ml of distilled water and weighed using analytical balance at determined period after the excess water was removed from the sample's surface. Using recorded data, the percentage of water retained (*S*) by each sample was calculated, according to Eq. (8):

$$S = \frac{m_s - m}{m} * 100 \quad (8)$$

where:

- m_s is the sample's mass at a defined immersion time (g),
- m is the initial mass of the sample (g).

2.3.9. Microbiological tests

To determine the surface contamination of analyzed samples, three types of tests were conducted:

- Swab Check test allows qualitative determination of total bacterial contamination. Microbiological tested surface is wiped with a cellulose buffer. Thus, any bacterium is transferred through the buffer in a special medium that contains a dye indicator. The tube is subjected to incubation at 37°C for 24h. A single bacterium is sufficient to cause a color change. This means that SwabCheck is about 1000 times more sensitive than conventional adenosine triphosphate ATP method. The benefits of the SwabCheck test are that it is sterile, packaged and ready for use. It is also easy to handle, provides fast results and has a long life. SwabCheck is used as an indicator of hygiene for different surfaces. Color change from red to yellow indicates a microbiological contamination. The change in color is based on the reaction of the acid from the medium composition with the pointer. A quick change in color indicates high levels of bacteria in the tested sample. SwabCheck is useful in determining levels of sanitation of surfaces in areas of food processing, beverage, dairy factories, restaurants, hospitals, microbiology laboratories etc.

- Contact plates tests allow determination of the total number of germs (NTG) and the number of *Enterococci* from the surface of the analyzed material. Contact plates are provided on each side with a slide containing culture medium. Slides are placed in plastic tubes, fitted with a lid.

The medium on one side is Plate Count Agar, orange, to determine the total number of germs, and on the other side is VRBG Agar (Violet Red Bile Glucose) Agar, red, for determining *Enterococci* (Fig. 1). Bacteria and fungi on tested surfaces are put on slides surface. The tubes where the blades are inserted are subject to incubation for 24-48 hours, and the results are compared with images of the diagrams in Fig. 2. Results are expressed in CFU/cm^2. The slides are compared to charts after 24 hours, reintroduced in the incubator and compared again after other 24 hours.

Fig. 1. Contact plates tests

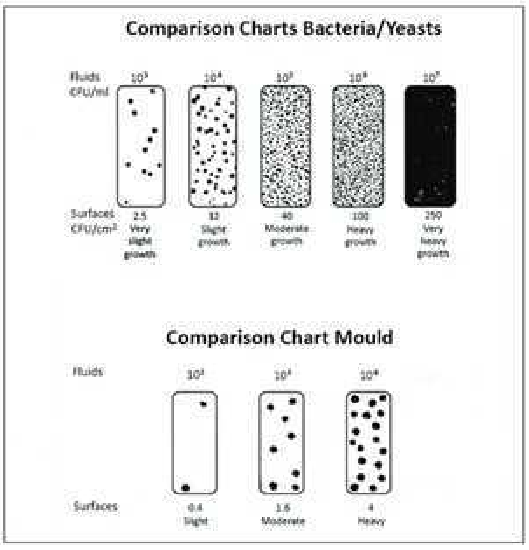


Fig. 2. Comparison charts bacteria (Dipslides for industrial and Environmental Monitoring of Bacteria and Fungi, Prospect, VWR International GmbH, Wien, Austria)

Each polymer sample was brought in contact with both sides of the plate. The plates were placed in plastic tubes and then were subjected to incubation at 37°C for 24 and 48 hours respectively, after which they were compared as in Fig. 2.

- *E. coli* test determines quantitatively the number of colonies of *E. coli* developed over the surface. This test uses a reference stock culture to obtain pure populations of individual microorganisms with known and predictable growing demands, with selective and differential properties, with biochemical or phenotypic activity, serological, response tests, known antimicrobial susceptibility features that are reproducible to authentic reference cultures.

a) Achieving primary culture

Kwik-STIK *E. coli* ATCC 25922 unit was left open at room temperature for thermal equilibration. Kwik-STIK unit is removed and stuck to the primary agar plate for identification. The gelatin tablet is positioned at the bottom of the device and the hydrating fluid reservoir is positioned on top of the device. The hydration fluid is released and then immediately the inoculation material is transferred on the agar medium with nonselective growth (primary culture). The inoculated area is stroke off 10-20 times with a sterile loop and then the rest of the agar surface is stroke off to obtain isolated colonies. The medium is immediately incubated, which determines the selection of representative well insulated colonies, to be used for transfers in Petri plates where the polymer samples will be applied.

b) Achieving the secondary culture

On the seventh day since processing reference strain for obtaining primary culture, a test culture in nonselective agar medium is prepared: representative, well isolated colonies from primary culture are harvested with a sterile loop and are dispersed on the medium, inoculating a circular area with a diameter of 25 mm and then stroke off 10-20 times the inoculated area to get isolated colonies. The subculture is then incubated for 24 hours at 37°C.

c) Inoculation

The previously obtained subculture is used for seeding the Petri plates in which SOY AGAR Tryptone medium was previously introduced. Seeding was done as follows: lactose-positive bacteria colonies, which were previously heated at 37°C for 2 hours, are inoculated on plates with a flamed loop. A sample of polymer was placed in each Petri box. They were incubated for 24 h at 37°C. After incubation results were evaluated by determining the number of colonies developed.

3. Results and discussion

Identification and quantification of components from polymeric waste led to the following results regarding the composition of the analyzed samples (Figs. 3-5).

As shown in Fig. 3, the main component of the municipal plastic waste is PE (59.57%). PP is found in proportion of 20.45%, the remaining polymers (PS, Nylon, PA, PVC, PC, PET) being found as contaminants of POs (approximately 25%). Fig. 4 reveals that the PE and PP can be separated through flotation from the rest of higher density polymers, PS and Nylon being found in MW3-6 only at a rate of 1.57%. However, due to the small density difference between PE and PP, they cannot be separated through flotation in water. Fig. 5 represents the composition of the heavy fraction. It contains predominantly polymers with higher density than the POs but one must specify that they also entrain about 8% POs. Of these, the highest proportion are PET, PVC and PS.

Since practical applications of products made from polymers require a good mechanical strength, tensile tests for both virgin polyolefins and samples made from waste were performed. The results are presented in Table 1. Note that MW3-6 fraction, predominantly consisting of POs, shows the best strength. The sample is stiffer than virgin polymers; it shows a higher elasticity modulus and a substantially lower relative elongation than polyethylene, but close to that of PP. This is possible due to the crosslinking between oxidized groups of the components as well as between unsaturated groups (vinyl) formed during life cycle. Tensile strength is close to that of PE, as dominant component of the fraction.

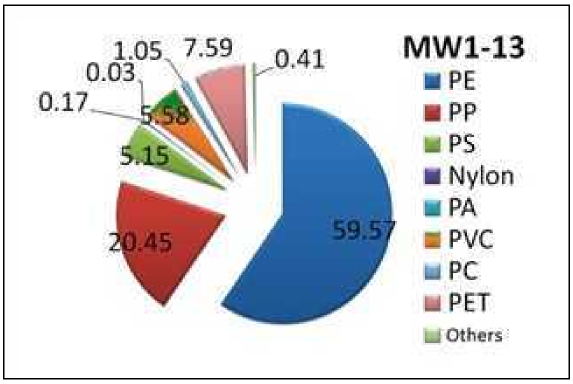


Fig. 3. Composition of MW1-13

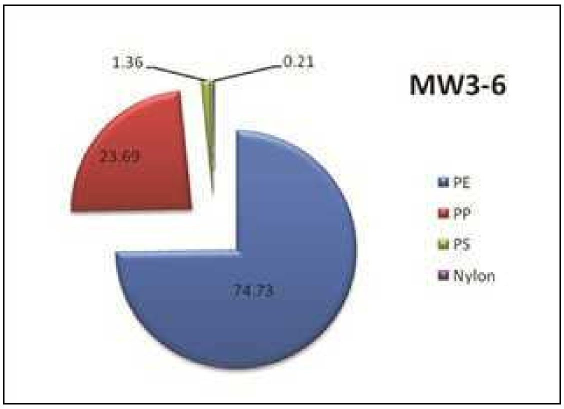


Fig. 4. Composition of MW 3-6

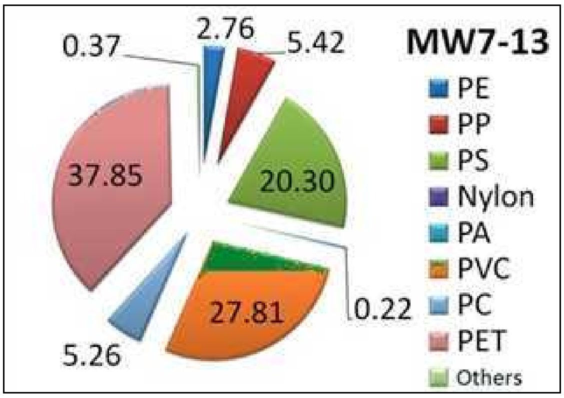


Fig. 5. Composition of MW 7-13

Currently products on the market made from composite materials are used on paneling, panels, flooring with similar properties (http://www.kedel.co.uk/). MW7-13, heavy fraction, considered a contaminant for POs, because of its very complex composition, because of incompatibility of polymers and because of very different degradation and melting temperatures, which does not allow the melting temperatures to ensure homogenization, shows the weakest mechanical properties. MW1-13 un-separated mixture, due to the POs content, shows mechanical properties similar to PE but the relative elongation is much smaller. Mechanical properties obtained for both materials prepared out of MW1-13, but especially those prepared out of MW3-6 encourages their proposal for various practical applications.

Good mechanical properties of materials made from wastes are not the only ones that can ensure the development of their practical applications. Inhibition of bacteria proliferation on their surface is another important aspect for use in common areas of human activity. Among the factors that influence the growth and adhesion of bacteria to the surface material could be mentioned: chemical composition, surface electric charge, hydrophobicity, surface roughness or surface typical configuration (Katsikogianni and Missirlis, 2004) Although POs are by definition hydrophobic materials, however FTIR spectroscopy has shown that virgin POs undergoes minor thermal oxidation during processing, that leads to the formation of polar groups OH (υ = 3400 cm^{-1}) and C = O (υ = 1510-1800 cm^{-1}) (Fig. 6) (Pavia et al., 1996).

These favor adsorption of water vapors from the atmosphere on the samples surface. After performing ATR FTIR analysis on samples maintained in laboratory atmosphere (humidity 45 ± 5%, temperature 25 ± 2°C) and on samples conditioned at 25°C in desiccator with CaCl$_2$, one may observe a change in the intensity (area) of absorption band from 3400 cm^{-1} (Table 2). Adsorption of water vapors at the surface may promote further growth of bacteria. From Table 2 it could be also noted that HI for wastes based materials is in the same range of magnitude with POs' HI. CI is much smaller than that of virgin POs suggesting a thermal degradation of wastes based materials during the thermal processing that follows a mechanism similar to Norish I. This statement is sustained also by comparing the determined average carbonyl index of MW1-13 before (0.72) and after thermal processing (0.1). The decrease of carbonyl groups number after thermal processing is due to the CO release (similar to Norish I photo-degradation mechanism). These results are in good agreement with those recently reported by Gardette et al. (2013) that show that both photo and thermal oxidation of polyolefins lead to the same products, only the relative concentrations of these products are dramatically different in the two processes.

The wetting ability of the surface can be evaluated by contact angle measurements.

Table 1. Mechanical properties of virgin POs and wastes fractions

Sample	***Young Modulus (MPa)***	***Tensile strength (MPa)***	***Elongation (%)***
LDPE	261.77	13.23	269.54
HDPE	738.16	25.87	393.41
PP	1153.65	31.63	5.09
MW1-13	587.29	13.60	0.70
MW7-13	1007.73	6.72	0.29
MW3-6	1466.77	18.15	1.10

Table 2. Area of the absorption bands characteristic for OH and C=O groups, hydroxyl index and carbonyl index of materials based on virgin POs and wastes

Sample	***A_{OH} (au)***		***HI***	***ΔA_{OH} (au)***	***$A_{C=O}$ (au)***	***CI***
	A_{lab}*	***A_{dry}*****				
LDPE	210	150	0.17	60	1265	2.14
HDPE	300	290	0.3	10	410	2.26
PP	160	150	0.04	10	233	0.55
MW1-13	170	-	0.11	-	160	0.10
MW7-13	302	-	0.22	-	252	0.18
MW3-6	136	-	0.23	-	84	0.14

**A_{lab} is the area of the OH absorption band for the sample conditioned in the laboratory atmosphere;*
***A_{dry} is the area of the OH absorption band for the sample conditioned in dried atmosphere (dessicator).*

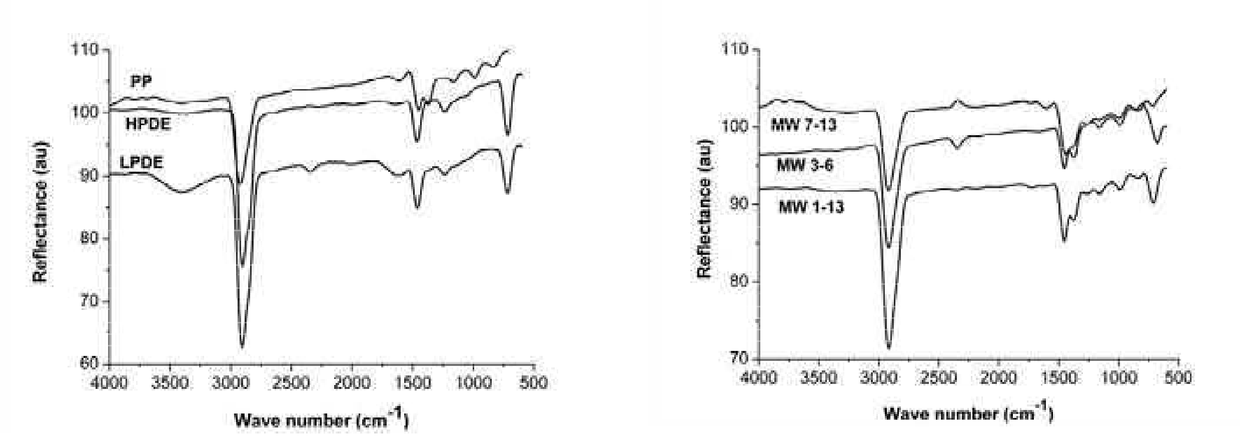


Fig. 6. FTIR ATR spectra for virgin PO and for tested waste fractions

Using experimental values of the contact angle one may calculate the surface energy of the samples. Thus, it was determined that LDPE and HDPE have similar values of surface energy (38.13 and 38.28 mN/m, respectively) while PP shows a lower value (36.29 mN/m), which demonstrates a more pronounced hydrophobic PP. In all cases, the dispersive component is dominating (85-90%).

In the case of waste, there is a noticeable decrease in surface energy as follows: MW3-6=17.8 mN/m, MW1-13 = 23.5 mN/m and MW7-13 = 26.5 mN/m. These values show a more pronounced hydrophobic behavior than virgin POs probably due to crosslinking or to elimination of polar groups obtained either by photo-oxidation occurring during the life cycle or due to thermal reprocessing. Dispersive component remains dominating (75-85%) but decreases compared to materials obtained from virgin polymer in favor of the polar component. The resulted values show a more pronounced decrease of surface energy as the content of the POs increases. This happens due to prevailing thermal degradation of POs through mechanisms similar to Norish I which consists of the elimination of CO or their crosslinking.

In general, hydrophobic bacteria better adhere to hydrophobic surfaces. However, tests show that the hydrophobicity of material's surface plays the most important role in bacterial adhesion by comparing to the bacterial surface hydrophobicity (Katsikogianni and Missirlis, 2004). Considering the obtained results, materials prepared from wastes (more hydrophobic) should favor bacterial growth compared to those obtained from virgin polymers (more hydrophilic). In the same time, it was determined that Gram negative bacteria (such as *E. coli*) are more hydrophilic then Gram positive bacteria (Sivakumar et al., 2010). So, they better adhere on more hydrophilic surfaces, in our case, on HDPE samples. By using the Lifshitz-van der Waals and Lewis Acid-Base (LW / AB) approach one may determine the surface electric charge of the material. The obtained values for Lewis base components (γ^-) are dominating compared to Lewis acid components

(γ^+) and vary depending on the composition of materials obtained from wastes as follows: MW1-13 = 3.42 mN/m; MW7-13 = 7.43 mN/m and MW3-6 = 16.49 mN/m. Note that the surface of materials is predominantly negatively charged. This reduces the ability of negatively charged bacteria to adhere to the surface of materials even if their hydrophobic behavior is emphasized. Taking into account that bacteria preferentially adhere and colonize porous surfaces (Katsikogianni and Missirlis, 2004), it was determined the roughness of samples obtained from polymeric waste included in the study.

AFM measurements of roughness reveal average values for virgin POs (ie 87.2063 nm for PP), higher values for MW3-6 fractions (207.47 nm) and MW7-13 fractions (170.15 nm) and lower values for fractions MW1-13 (27.85 nm). According to previous studies reported in the literature (Katsikogianni and Missirlis, 2004), more pronounced roughness increases the contact surface with the medium favoring bacterial growth. However, if the conformation of roughness does not dimensionally fit the characteristics of bacteria then it reduces the contact surface of bacteria with the material and their adhesion is hindered (Fig. 7). Tests applied to bacterial growth on the surface of studied materials led to the results shown in Table 3.

Significant images of the microbiological tests are presented in Fig. 8.

Higher resistance of materials obtained from waste to bacterial growth can be explained by the fact that while sheet samples made from virgin POs were obtained in the laboratory without supplementary additives than antioxidant, materials obtained from waste may also contain antibacterial (nisin, naftamicyn) or bacteriostatic substances, used in the initial processing, especially for food packaging, which still retain their activity after one product life cycle.

Antibacterial substances are generally added in a small amount and that makes them undetectable by FTIR spectroscopy. Also, a number of dyes (methylene blue, Blue Toluidines A) and pigments (ZnO and TiO_2) used to develop packaging, may have antimicrobial behavior and impart this behavior to polymeric waste that contains them. Both in the heavy fraction MW7-13 and in the un-separated waste, PVC has been identified. Its presence and possible degradation during the life cycle can generate HCl or chlorine based compounds showing antibacterial nature. The "others" category highlighted of plastic waste composition (Figs. 3 and 5) may also include acrylic esters commonly used as adhesives for labels. They are also known as antibacterial substances. Thus, small amounts of antimicrobial agents coming from different antimicrobial packaging may exercise their character, even synergistically in materials obtained from waste. Also, increased stiffness of materials coming from waste (a high Young's modulus) determines the impossibility of multiplying bacteria initially attracted by the rough surface, because of hindering their elongation as essential step in cell division (Bonilla and Fernández-García, 2012).

Changes in polarity and crystallinity of materials also influence sorption of water during material's immersion. The small amounts of water adsorption (0.1-2.38%) are characteristic to hydrophobic and highly crystalline materials. This aspect highlights the reduced possibility of polymer structure swelling by adsorption of water and thus the reduced release of antibacterial agents from the polymer matrix during the life cycle, respectively during washing and separation by flotation method. This argument is in favor of maintaining antibacterial agents in the material for a long time, even after it became waste.

Thus, by DSC measurements it was obtained a higher crystallinity index in the case of virgin polymers: HDPE (69.72%), PP (42.02%) and LDPE (36.77%) than in the case of waste based materials. The fraction containing the most POs, MW3-6, has the highest crystallinity index (29.11%) while the waste undivided into fractions reveals a lower crystallinity index of 15.39%. For the contaminant fraction, by DSC, it was impossible to determine this feature, as the thermogram highlighted predominantly amorphous character. The same issues can also be highlighted by X-ray diffraction which determines the total crystallinity of samples (including inorganic additives). Thus, according to XRD analysis, in the case of wastes, the highest crystallinity was obtained for fraction MW3-6 (76.91%) and the lowest for the sample obtained from contaminant fraction MW7-13 (50.88%). The high crystallinity obtained for waste materials is consistent with the low values of their water adsorption (0.89-2.38%) and suggests the minimum possibility of releasing the antimicrobial agents from their structure.

Table 3. Results of microbiologic test

Sample	*Swabcheck*	*NTG (CFU/cm^2)**	*Enterococci (CFU/cm^2)*	*E. coli (CFU/cm^2)*
LDPE	-	0	0	0
HDPE	+	4	0	1 (around the sample)
PP	-	1	0	0
MW1-13	-	0	0	0
MW3-6	-	0	0	0
MW7-13	-	0	0	0

**CFU_colony-forming unit*

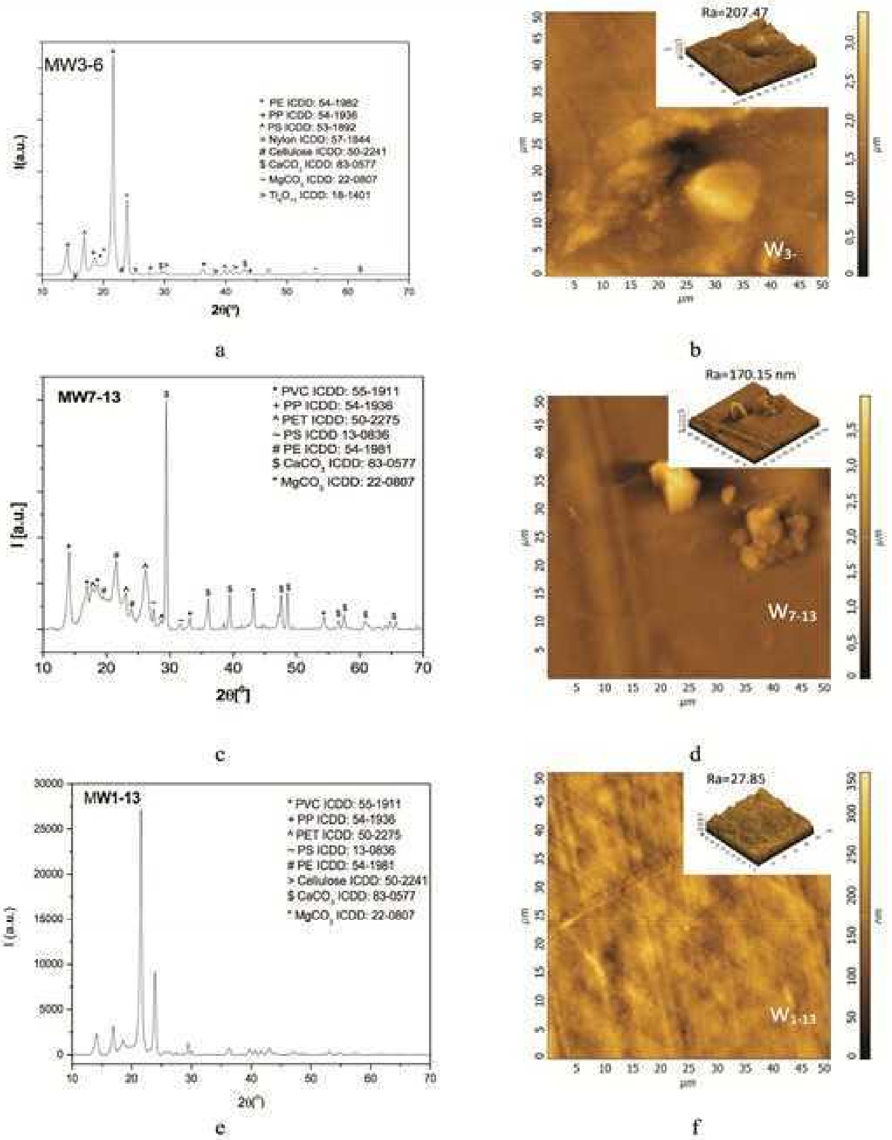
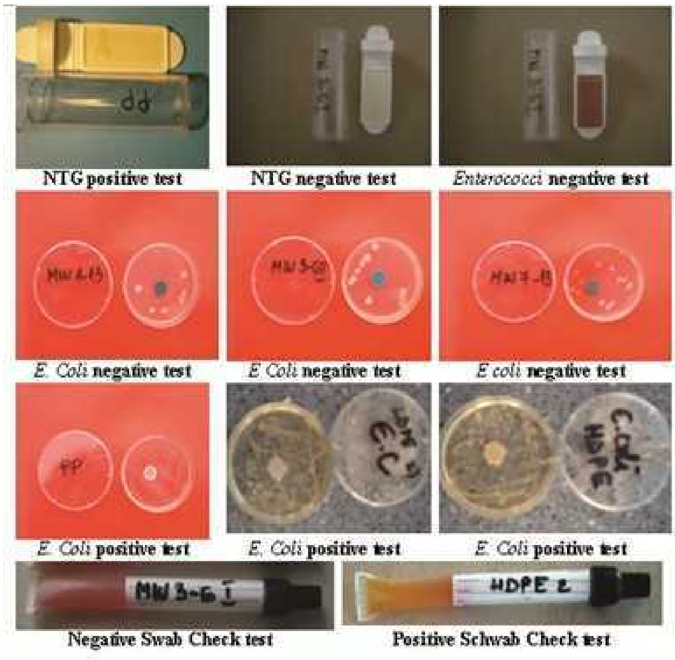


Fig. 7. XRD and AFM characteristics of the waste based materials


NTG positive test NTG negative test *Enterococci* negative test

E. Coli negative test *E. Coli* negative test *E coli* negative test

E. Coli positive test *E. Coli* positive test *E. Coli* positive test

Negative Swab Check test Positive Schwab Check test

Fig. 8. Significant images of microbiology tests

4. Conclusions

The present study highlighted that the surface of materials obtained from polymeric wastes by melt-mixing and pressing does not allow bacteria (*E. coli* and *Enterococci)* and germs (NTG) to adhere and colonize.

Materials obtained from waste seem to be sanitary safe and could be used for obtaining products that are commonly used by many people, without any contamination risk with the tested bacteria and germs. This property is due to: (1) the reduced capacity of materials based on wastes to swell in water or atmosphere moisture, minimizing the release of the small amounts of antimicrobial agents initially introduced into packaging materials; (2) high material hydrophobicity; (3) low negatively charged surface that repels the negative charged bacteria; (4) surface conformation that even rough seems to be not fitted with the tested bacteria shape and dimensions; (5) material rigidity that hinders the eventually adhered bacteria into grooves and scratches to elongate in order to divide and colonize the surface.

Future studies have both to enlarge the tested bacteria areas, aiming to confirm the microbiological safety of the materials based on wastes and to get more insight information concerning the stability of antimicrobial agents at the end of life cycle of polymeric materials.

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