



“Gheorghe Asachi” Technical University of Iasi, Romania



COLORS DISTRIBUTION IN POLYMER WASTES AND COLOR PREDICTION OF RECYCLED POLYMERS

Silvia Patachia¹, Catalin Croitoru^{2*}, Liana Baltes², Mircea Tierenan²

¹Product Design and Environment Faculty, Transilvania University of Brasov, 29 Eroilor Str., 500036 Brasov, Romania

²Materials Science and Engineering Faculty, Transilvania University of Brasov, 29 Eroilor Str., 500036 Brasov, Romania

Abstract

In this paper, several image analysis techniques have been applied aiming to obtain useful information regarding the processing of municipal solid waste polymers. An automated color extraction method has been applied in order to quantize the color distribution in the polymer wastes aiming their resource and time-efficient separation according to their color. Also, by processing different density fractions from the polymer waste the color of the final material has been predicted, as well as the potential degradation of the material in the processing conditions used in the study. The image analysis techniques used in this paper could complement other polymer characterization techniques and could lead to an increase in the efficiency of waste recycling management by efficiently planning-ahead of the processing parameters and of the raw materials used (dyes, pigments).

Key words: colour distribution, image analysis, polymer composite, polymer waste, separation

Received: February, 2016; *Revised final:* October, 2016; *Accepted:* December, 2016; *Published in final edited form:* May 2019

1. Introduction

Plastic wastes coming from different sources are characterized both by polymers and additives nature (Delva et al., 2018; Korhonen et al., 2004; Luca and Ioan, 2014; Singh and Pant, 2018). Separation of polymers can be made both by using differences of their density and of their specific absorption in IR domain, the sorting results consisting in several masses, each comprised of one variously colored polymer (Dijkema et al., 2000; Hidalgo et al., 2014). Traditionally, in order to ensure the maintaining of the recycled polymer characteristics constant is to make it all black (Bartolacci et al., 2017). Black pigments are very good at masking other colors underneath and contaminants (Rem et al., 2009; Ropota et al., 2009). But nowadays, black color is not a desired one in view of new product designing. That is why, new methods of polymer wastes separation based on their color gain importance (Heidrich and Harvey, 2018; Rochman et al., 2013; Toldy et al., 2009). Color sensors and

processors have been developed, their current generation being capable of detecting and electronically classifying millions of pixels and tens of thousands of plastic flakes per second into many different categories (Haupt et al., 2018; Scott, 1995). However, mechanical blow-bar technology, which is used to extract the classified material, is able to process only thousands of flakes per second without introducing very high contamination levels in product streams. These blow bar systems are thus too slow and clearly a bottleneck in sorting. They are sensitive to sorter errors, operationally expensive and their cost is scaling proportionally with the number of products extracted from a stream, unfortunate for polymers, which are present in many different shades of color (Rochman et al., 2013; Serranti et al., 2015).

The aim of this paper is to demonstrate the effectiveness of different image analysis techniques in quantifying the distribution of colors in the initial mixture of plastic wastes, in quantifying the effectiveness of their separation by color and to

* Author to whom all correspondence should be addressed: e-mail: c.croitoru@unitbv.ro; Phone: +40748126598

predict the color of plastic obtained by reprocessing of each fraction. The proposed method could take into account also the degradation of polymers and dyes or pigments both during the life cycle of the polymers but also due to the reprocessing.

2. Materials and methods

2.1. Materials

Municipal solid wastes (MSW) samples comprising of plastic flakes with different composition and colors have been provided by Urban Brasov, from Brasov County, Romania and were further used as mentioned in section 2.2.

Ethanol 96% wt., NaCl and Na₂CO₃ have been purchased from Sigma-Aldrich and used as such for the preparation of aqueous solutions with determined density values, used for MSW separation in density fractions, as described in section 2.2.

Polypropylene grafted with maleic anhydride (PP-MA; average Mw ~9,100 by GPC, average Mn ~3,900 by GPC, maleic anhydride 8-10 wt. %) and polyethylene grafted with maleic anhydride (PE-MA; viscosity 1,700-4,500 cP (140 °C)) have been purchased from Sigma-Aldrich and have been used as coupling agents in the process of polymer composites obtaining.

Octodecyl-3(3,5-ditertbutyl-4-hydroxyphenyl)propionate (Irganox1076) has been purchased from Sigma-Aldrich and used as thermal stabilizer in the process of polymer composites obtaining.

2.2. Methods

2.2.1. Polymer waste treatment and separation

The MSW sample, washed several times with detergent (branched dodecylbenzenesulphonate) and distilled water in order to remove dirt and other contaminants (W1-13), has been separated by means of the flotation method in 13 density fractions, with the gravimetric composition and density interval (expressed in g/cm³) as illustrated in Fig. 1. Aqueous solutions of ethanol (for the fractions with density lower than 1 g/cm³), sodium carbonate and sodium chloride (for the fractions with density higher than 1 g/cm³) have been used as flotation liquids (Moldovan, 2012; Moldovan et al, 2013).

The photographic images of the MSW and of the separated density fractions respectively, have been obtained with a Sony DSC110 H-20 digital camera, at 3072x2034 pixel resolution, under identical camera settings, ambient light conditions and distance from the camera objective to the sample (20 cm). The illumination conditions have been kept the same for the photographing of each polymer waste type and the photographed area has been chosen appropriately in order to be fully covered with plastic flakes, in order to eliminate background effects.

2.2.2. Polymer composites obtaining

Different MSW fractions have been finely ground in particles with 0.5-1 mm average linear dimensions by using a Netzsch ZM100 centrifugal mill. The composite materials have been prepared either by using the unseparated MSW (W1-13), either by mixing the components from fractions W7-13 in melted form, in a determined amount, by using an internal mixer (Brabender lab station) with a rotor speed of 60 rpm for 10 minutes. The W6 density fraction has been used as such, since it is the majoritarian component from the polymer waste.

The working temperatures have been set at 180 °C for the fraction with majoritarian PO composition (W6), and 220 °C for the W1-13 and W7-13 fractions, with components having higher average melting temperatures. For the obtained materials, 0.5% wt. Irganox1076 and 5% wt. compatibilizer (PP-MA for W1-13, PE-MA for W6) has been added in the polymer melt. The obtained polymer mixture has been cooled to room temperature, cut and pressed into 150x150x1 mm forms with the help of a hydraulic press with preheated plates.

2.2.3. Image analysis

2.2.3.1. Identification of polymer fractions composition

As it could be noted from Fig. 1, each fraction is formed by pieces of polymers having different colors. Taking into account that each fraction corresponds to a quite narrow interval of density, based on our prior experiments (Patachia et al., 2011) it has been assumed that in the lower fractions, rich in polyolefins, the same color corresponds to the same polymer inside a certain density fraction.

Regarding the fractions presenting a relatively low amount of polymer types in composition, by analyzing the polymer type of each representative color and quantizing the percentage distribution of each color in the analyzed image as ratio of the pixel occupied by a certain color reported to the total number of pixels from the image, it could be possible to assess the compositional distribution of each polymer type in a certain density fraction.

In our previous studies, image analysis has been performed in order to determine the percentage of each color from different types of polymer wastes, by means of Adobe Photoshop CS5 software (Patachia et al., 2011). However, this method, albeit being simpler and cheaper than other traditional color quantizing methods, has the disadvantage that it is rather time-consuming, owing to the manual selection of each color hue from the photographic images of the polymer wastes. In this study, executing a PHP programming language script (<http://www.phpclasses.org/package/3370-PHP-Extracts-the-most-common-colors-used-in-images.html>) has been used as an automated color extraction approach. The adapted script can be used to extract the most common colors from an image.

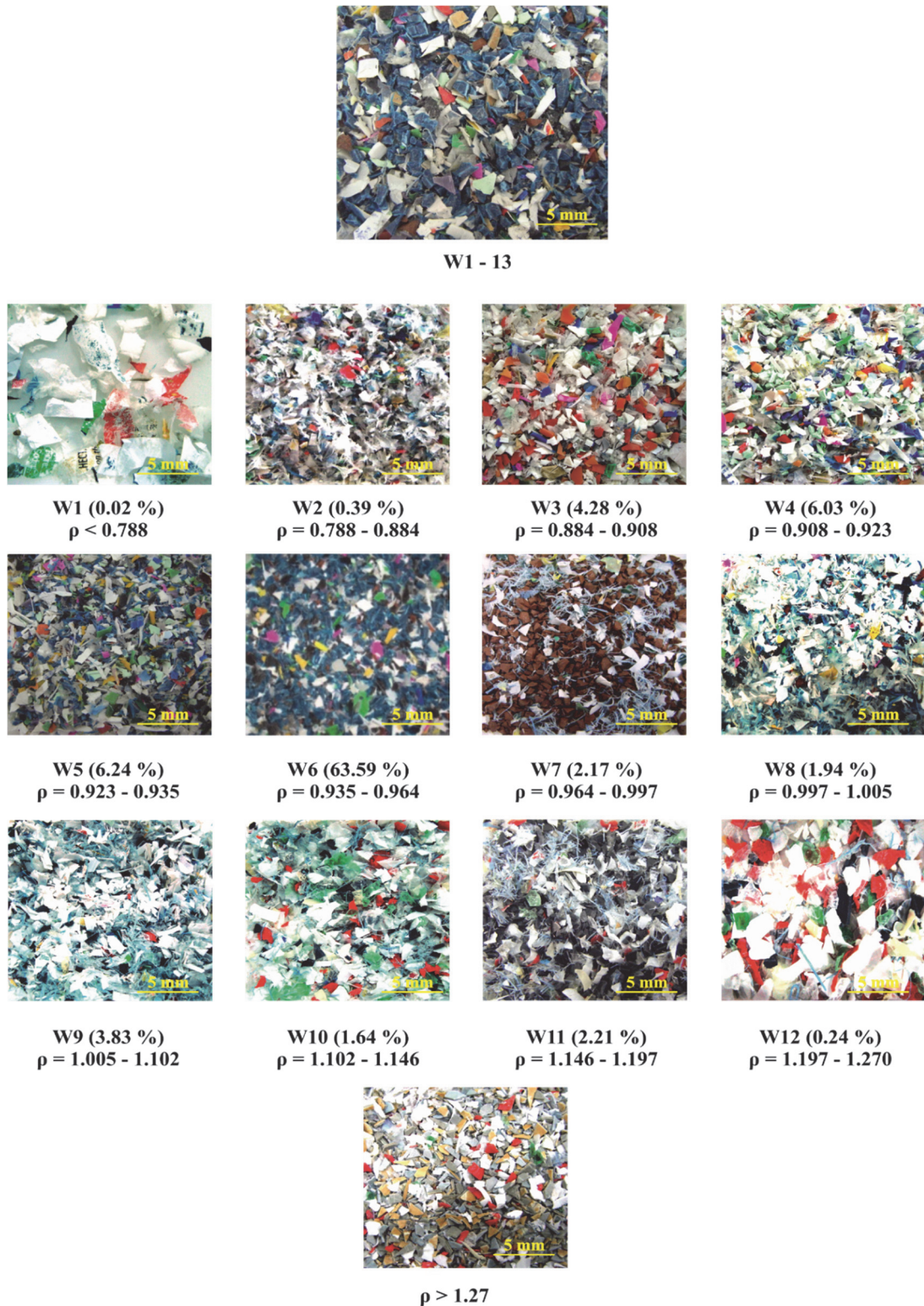


Fig. 1. MSW wastes separated in density fractions by the flotation method (density units: g/cm^3)

Running the script requires the following parameters (Fig. 2):

- image - the filename and location of the image (loads the image to be quantized);
- count - how many colors should be returned (0-255). Zero value has been used in this study, meaning that all colors have been extracted.

- delta - the amount of gap when quantizing color values (0-255). Lower values mean more accurate colors. The default value of 16 has been used.

The script returns the quantized colors as HEX color codes (formed of six characters) and the fraction of each found color (0 to 1), reported to the total area (in pixels) of the image, as it can be seen from Fig. 2.

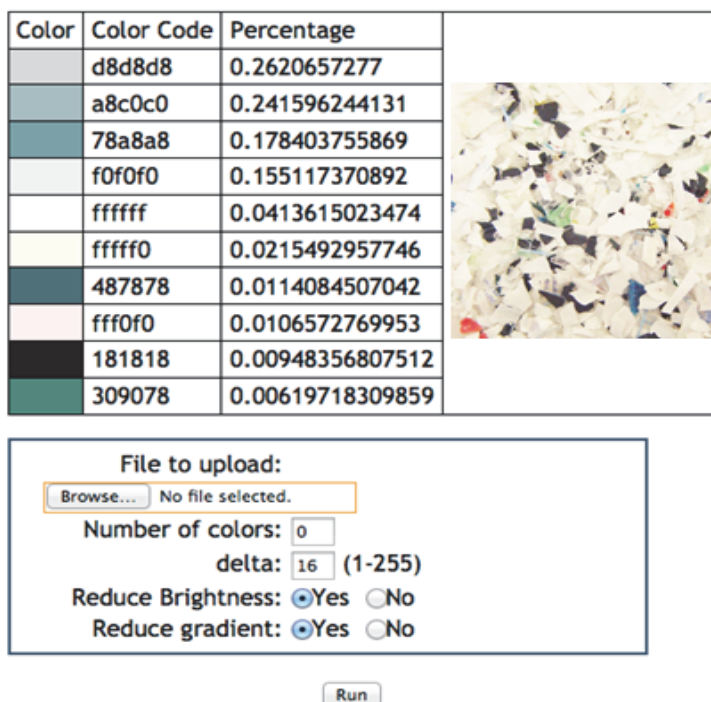


Fig. 2. Example of PHP script working screen

In order to determine the percentage distribution of polymers in each density fraction based on the analysis of their color distribution, the following work steps have been employed:

i. From each density fraction a determined number of polymer pieces (minimum 30) from each chosen color has been analyzed by FTIR spectroscopy by using a Perkin-Elmer BXII Fourier transform infrared spectrometer, equipped with an attenuated total reflectance (ATR) device, with a resolution of 4 cm⁻¹ in the 4000-600 cm⁻¹ interval.

ii. To identify the types of chosen representative polymers from each fraction and corresponding to each representative color, the FTIR spectra of the polymers, obtained according to (i.) have been compared with several polymers standard spectra from FDM Spectral Libraries (organic polymers), a part of Essential FTIR software. Identification of the polymer type has been performed based on the highest value of the correlation coefficient, computed by the software. For each density fraction, the type of polymer corresponding to each color has been determined. The assumption that a polymer type could be ascribed to a certain color has been verified by performing FTIR analysis on at least 30 flakes of similar color (same RGB values, ± 0.5%) from each density fraction.

iii. For a chosen density fraction, its percentage composition has been determined by summing up the percent of each found color, computed by the PHP color extraction script that corresponds to a type of polymer (providing that a type of polymer can be found in several colors in a certain density fraction).

2.2.3.2. Color prediction of polymer composites

In principle, the theoretical color of the composites has been computed by employing the following work steps:

(a): HEX color codes provided by PHP program for each density fraction converting into an R(red), G (green) and B (blue) array with the help of Microsoft Office Excel software package. The values for R, G and B are integers ranging from 0 to 255. The advantage of using the RGB color system is that every color can be expressed in computer terms as a combination of red, green and blue in different proportions. For example, (0,0,0) corresponds to black, (255,255,255) corresponds to white, (255,0,0) corresponds to red, and so on.

(b): Calculating the (R,G,B) for the composite, as the weighted arithmetic mean of the R,G,B values for each color and each density fraction, taking into account the color distribution percent in each fraction (provided by the PHP program) and each density fraction gravimetric composition:

i. For the composites obtained from the unseparated MSW1-13 wastes and those obtained from a single density fraction, the (R, G, B) array could be calculated with Eq. (1):

$$(R, G, B) = \sum_{i=1}^N f_i \cdot (R_i, G_i, B_i) \tag{1}$$

where: N= total number of colors identified to which also the colored additive (coupling agent) is counted;

(R_i, G_i, B_i) = red, green and blue components for each identified color;

f_i = fraction for each identified color, including that of the coupling agent (calculated as color percent/100)

ii. For the composites obtained from mixing different separated density fractions, the (R, G, B) array could be calculated with Eq. (2):

$$(R, G, B) = \sum_{j=1}^K \sum_{i=1}^N g_j \cdot f_i \cdot (R_i, G_i, B_i) \quad (2)$$

where: K = number of mixed density fractions

g_j = gravimetric fraction of added density fraction (gravimetric percent/100)

2.2.3.3. Quantization of polymer degradation during composites processing

During the preparation process, the MSW polymers could suffer degradation of either the polymer matrix (chromophore groups and/or multiple bonds formation), as well as of the dyes and pigments that each individual polymer particle contains.

In this study, the color differences of the obtained composites in comparison with the predicted (theoretical) colors, obtained as described in section Color prediction of polymer composites have been assessed by image analysis using the CIELAB color system. CIELAB describes accurately and objectively all the colors visible to the human eye and was created to serve as a device-independent model to be used as a reference in photography and colorimetry. It uses three coordinates, namely: the lightness of the color (or luminosity) L^* , ranging from black (0) to diffuse white (100); a^* -which indicates the color positioning between green and red (negative a^* values indicate green hues while positive values indicate red hues) and b^* -which indicates the color positioning between yellow and blue (b^* , negative values indicate blue and positive values indicate yellow) (Zhang and Wandell, 2012).

The photographic images of the composites have been obtained as described in section 2.2.1, and the values of L^* , a^* and b^* have been determined with Adobe Photoshop software, version CS5, by using its color palette. The differences between the values of the L^* , a^* , b^* parameters (P) for the composites and the reference (predicted theoretical color) have been determined by using Eq. (3):

$$\Delta P^* = P_{composite}^* - P_{reference}^* \quad (3)$$

With the help of the parameters difference, the total color difference (ΔE) could be calculated (Eq. 4):

$$\Delta E = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \quad (4)$$

3. Results and discussions

The extracted color hues obtained by running the PHP script with the photographic images corresponding to each separated density fraction from Fig. 1 are illustrated in Fig. 3. It could generally be

seen from Fig. 1 that the lighter MSW fractions (W1-5) are dominantly composed of different flakes of transparent polymer foil, preferentially distributed at the surface of the separated MSW fraction, the majoritarian being colorless, white and blue-grey. These transparent flakes can cover other colored polymer flakes, and the PHP color extraction program identifies them as bearing different shades of grey, depending of the color of the covered particles. For the light MSW fractions is thus difficult to accurately predict the distribution of each color. In this case a visual inspection of the polymer waste is needed, in order to discriminate between transparent flakes and true grey polymer flakes.

In the heavier fractions, W6-13, the percentage of transparent particles is more reduced, thus the method of color extraction providing more accurate results. The dominating color hues are red for the W7, blue for the W6 fraction, and grey for W10, 11 and 13. W8-10 fractions are dominantly comprised of whitish polymer flakes, in accordance with the images presented in Fig. 1.

Since the W6 fraction has the highest gravimetric percent, the unseparated W1-13 polymer mixture is also dominating blue and grey.

The PHP color extraction script generates results comparable to the manual Photoshop color quantizing method (Patachia et al., 2011). Table 1 illustrates the color distribution of the W2 fraction obtained from Adobe Photoshop and PHP color extraction script, as well as of the identified polymer type, according to the procedure detailed in section 2.2.1. As it can be seen from Table 1, the results obtained from both methods are comparable. Generally, it could be noticed that the color extraction script is more sensitive to close color hues than Adobe Photoshop, which perceives a part of light grey or yellow as white. For both color-quantizing methods a visual inspection of the photographic images is needed, especially for the lighter fractions that are dominantly comprised of transparent foils and polymer flakes.

Fig. 4 presents the composition of the initial unseparated polymer waste material (MW1-13) and of different density fractions and mixtures of the separated fractions thereof (MW6, MW7-13) that have been used to obtain polymer composites. The composition of the aforementioned fractions has been determined by using the color distribution percent generated by the color extraction PHP script, as detailed in section 2.2.1. The majoritarian components of the municipal solid wastes are the polyolefins: polyethylene (PE) and isotactic polypropylene (PP); in the lighter fractions (W6) the dominating component is PE (especially low density PE); while in the heavier fractions (W7-13) the dominating components are poly (vinyl chloride) (PVC), polystyrene (PS) and polyamides (PA).

This color quantization method could thus prove useful in determining the overall composition of complex polymeric wastes, or in separating these wastes based on their color.

Table 1. Color distribution and polymers types identified in the W2 fraction

| Adobe Photoshop colour identification | | | | | PHP script | | | Identified polymer type* |
|---------------------------------------|-----------------------------|--------------------|--------------------|--------------|------------|--------------------|----------------------------|----------------------------|
| Total pixels of image | Colour | No. pixels/ colour | Colour percent (%) | σ (%) | Colour | Colour percent (%) | σ (%) | (Correlation coefficient) |
| 134320 | Trans-parent | 57552 | 42.84 | 2.79 | | 46.12 | 3.44 | PPi (Tg=-26) (0.989) |
| | Grey/white-transparent | 50517 | 37.61 | 4.53 | | 31.14 | 5.44 | PE (LDPE Mw=50000) (0.922) |
| | | | | | | 9.07 | 0.76 | |
| | White | 14023 | 10.44 | 0.31 | | 6.44 | 0.32 | PPi (Tg=-26) (0.915) |
| | Blue (caeru-lean) | 3223 | 2.40 | 0.38 | | 1.2 | 0.13 | PE (LDPE Mw=50000) (0.948) |
| | | | | | | 0.55 | 0.09 | |
| | Dark navy-blue | 2981 | 2.22 | 0.21 | | 1.48 | 0.12 | PPi (Tg=-26) (0.91-0.956) |
| | Light-blue transparent film | 402 | 0.30 | 0.03 | | 0.65 | 0.08 | |
| | Green | 2085 | 1.55 | 0.32 | | 1.44 | 0.12 | |
| | Vermi-lion red | 405 | 0.3 | 0.03 | | 0.2 | 0.08 | |
| Bor-deaux red | 1813 | 1.35 | 0.12 | | 1.44 | 0.11 | | |
| Mus-tard yellow | 805 | 0.60 | 0.08 | | 0.12 | 0.04 | PE (LDPE Mw=50000) (0.941) | |

*PPi: isotactic polypropylene; PE: polyethylene; LDPE: low density polyethylene; Mw: average gravimetric molecular mass; Tg: glass transition temperature. Correlation coefficient (between 0 and 1, related to the probability of polymer identification, higher the correlation coefficient, the higher the accuracy of the polymer identification)

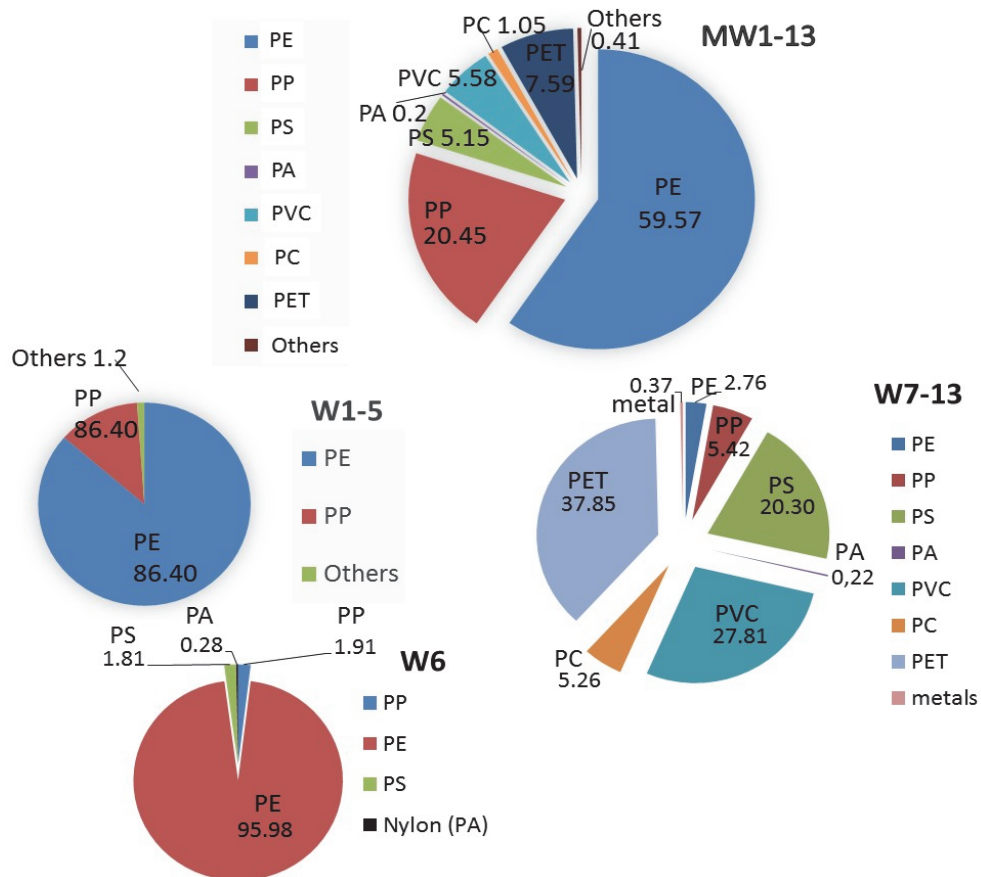


Fig. 4. Different MSW fractions composition

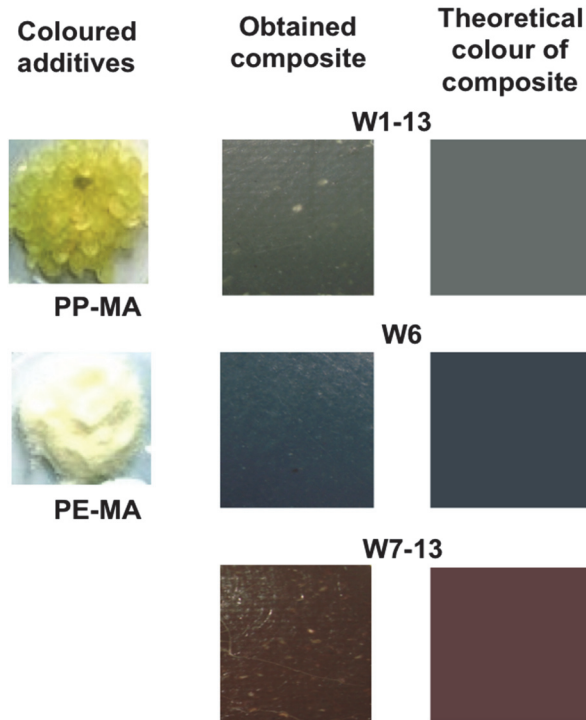


Fig. 5. Actual and predicted color of the MSW composites

Table 2. CIELAB color parameters of the polymer composites

| Composite type | Analyzed image | L^* | a^* | b^* | ΔL^* | Δa^* | Δb^* | ΔE |
|----------------|----------------|-------|-------|-------|--------------|--------------|--------------|------------|
| W1-13 | real | 47 | -7 | -5 | -5 | -3 | 3 | 6.55 |
| | predicted | 52 | -4 | 2 | | | | |
| W6 | real | 37.2 | -8 | -5 | 3.2 | -4 | 1 | 5.21 |
| | predicted | 34 | -4 | -6 | | | | |
| W7-13 | real | 39 | 14 | 16 | 0 | -3 | 9 | 9.48 |
| | predicted | 39 | 17 | 7 | | | | |

During processing, also a slight shifting of color towards green could be observed. This tendency is more pronounced in the case of W6 composite, obtained from a density fraction with dominating blue polymer flakes, so the reason for this behavior could be explained by the possible degradation of the blue pigment/dye in the polymer, possible reaction with other colored components from the system, lack of compatibility with other polymers or simply by “dilution” of the original color that occurs in the melt-mixing process as well as polymer degradation. Yellowing of polymers, due to their degradation, superimposed on the initial dominating blue color of the polymers waste will lead to a green color of the processed material.

This image analysis method could prove useful in characterizing the processing stability of the polymer wastes and could be useful in sustaining the information obtained from other methods of analysis, such as microscopy or FTIR spectroscopy.

Based on the values of ΔL^* , Δa^* and Δb^* the predicted color for the materials obtained in the case of several recycling processing steps of the initial composite could be also computed, according to Eq.

(5) and illustrated in Fig. 6.

$$P_n^* = P_{initial}^* + n \cdot \Delta P^* \tag{5}$$

where: P = colour parameters L^* , a^* and b^* ;
 n = number of recycling (processing) times;
 ΔP^* = values of ΔL^* , Δa^* and Δb^* from Table 2, for each material;

It could be observed from Fig. 6 that the material obtained from the unseparated W1-13 polymer darkens progressively with each reuse, having also a pronounced tendency to shift towards green hue, after a fourth reuse. Provided the same condition, the W6 composite has a pronounced blue shift after the third reuse and the W7-13 composite, a noticeable shift from sepia-brown towards ochre-brown.

4. Conclusions

This study demonstrates the application of several image analysis techniques in quantifying the colour distribution, composition and the modifications that occur during (re) processing of municipal solid waste polymers.

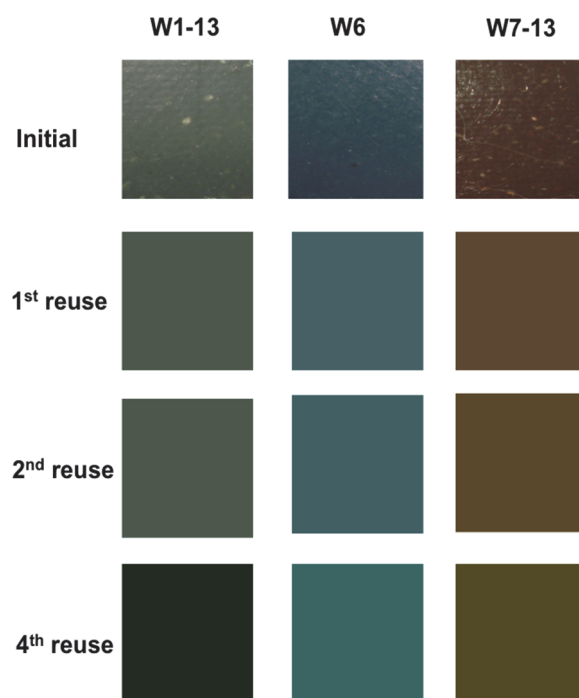


Fig. 6. Colour of MSW material after several times recycling

Also, by periodically analyzing the color modifications of a material exposed to outdoor conditions (especially of the a^* parameter) the degradation kinetic could be determined, which could provide useful information regarding the supplementary additivation of the polymers utilized under exposure to high temperatures, solar UV, humidity, wind, and so forth.

The proposed methods could prove useful in the field of polymer waste management and processing industry, due to its ease of use, possible integration in an automated (or semi-automated) workflow and its low cost, providing future insights on the renouncing of the black color for the materials obtained from plastic wastes, as well as the colors adapting for the design of new products.

Acknowledgements

This work was supported by a grant of the Romanian National Authority for Scientific Research and Innovation, CNCS - UEFISCDI, project number PN-II-RU-TE-2014-4-0173.

References

- Bartolacci F., Del Gobbo R., Paolini A., Soverchia M., (2017), Waste management companies towards circular economy: What impacts on production costs?, *Environmental Engineering and Management Journal*, **16**, 1789-1796.
- Delva L., Cardon L., Ragaert K., (2018), Evaluation of post-consumer mixed polyolefines and their injection moulded blends with virgin polyethylene, *Environmental Engineering and Management Journal*, **17**, 427-434.
- Dijkema G.P.J., Reuterb M.A., Verhoef E.V., (2000), A new paradigm for waste management, *Waste Management*, **20**, 633-638.
- Haupt M., Kägi T., Hellweg S., (2018), Modular life cycle assessment of municipal solid waste management, *Waste Management*, **79**, 815-827.
- Heidrich O., Harvey J., (2018), An examination into recycling and waste management attitudes and behaviors by UK employees, *Environmental Engineering and Management Journal*, **17**, 71-81.
- Hidalgo D., Corona F., Martín-Marroquín J.M., Gómez M., Aguado A., Antolín G., (2014), Integrated and sustainable system for multi-waste valorization, *Environmental Engineering and Management Journal*, **13**, 2467-2475.
- Korhonen J., Okkonen L., Niutanen V., (2004), Industrial ecosystem indicators- direct and indirect effects of integrated waste- and byproduct management and energy production, *Clean Technologies and Environmental Policy*, **6**, 162-173.
- Luca F.A., Ioan C.A., (2014), Implementation of green marketing in the analysis of municipal waste produced in Romania, correlated with environmental policy management. *Environmental Engineering and Management Journal*, **13**, 3131-3142.
- Moldovan A., (2012), *Composite materials based on polyolefin and cellulose fibres obtained from second raw materials*, PhD Thesis, Transilvania University of Brasov, Brasov, Romania (in Romanian).
- Moldovan A., Patachia S., Vasile C., Darie R., Manaila E., Tierean M., (2013), Natural Fibres/Polyolefins Composites (I) UV and Electron Beam Irradiation, *Journal of Biobased Materials and Bioenergy*, **7**, 58-79.
- Patachia S., Moldovan A., Tierean M., Baltes L., (2011), *Composition determination of the Romanian Municipal Plastics Wastes*, Proc. 26th Int. Conf. on Solid Waste Technology and Management, Philadelphia, U.S.A., 940.

- Rem P., Solaria V., Di Maio F., (2009), High-purity products from plastic waste: the W2Plastics project, *Environmental Engineering and Management Journal*, **8**, 963-966.
- Rochman C.M., Browne M.A., Halpern B.S., Hentschel B.T., Hoh E., Karapanagioti H.K., Rios-Mendoza L.M., Takada H., Teh S., Thompson R., (2013), Policy: Classify plastic waste as hazardous, *Nature*, **494**, 169-171.
- Ropota I., Zamfirache E., Muntean M., (2009), New composites from solid waste, *Environmental Engineering and Management Journal*, **8**, 931-933.
- Serranti S., Luciani V., Bonifazi G., Hu B., Rem P.C. (2015), An innovative recycling process to obtain pure polyethylene and polypropylene from household waste, *Waste Management*, **35**, 12-20.
- Singh P., Pant D., (2018), Waste-to-waste management and resource conservation and recycling. *Environmental Engineering and Management Journal*, **17**, 1103-1111.
- Toldy A., Bodzay B., Tiercan M., (2009), Recycling of mixed polyolefin wastes, *Environmental Engineering and Management Journal*, **8**, 967-971.
- Zhang X., Wandell B.A., (2012), A spatial extension of CIELAB for digital color-image reproduction, *Journal of the Society for Information Display*, **5**, 61-63.

Web sites:

<http://www.phpclasses.org/package/3370-PHP-Extracts-the-most-common-colors-used-in-images.html>