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COMPARISON OF THE STANDARD AND RECYCLED PE 3-LAYERED FILMS

ABSTRACT

The work presented in this article focuses on the analysis of the structure and properties of newly developed 3-layer composite films produced using blow moulding technology supported by a precision gravimetric dispensing system. In order to assess the influence of the addition of regranulate on the properties of the films a number of tests and studies were carried out including differential scanning calorimetry, spectrophotometric tests and weld break force test called hot tack. bservation of hot tacktest was performed using stereoscopic microscopy. As part of the research, three-layer LDPE (Low-Density Polyethylene) films were produced with the proposed layer distribution: A- 20%, B-60%, C-20%, with varying amounts of recycled PE (RPE) and calcium carbonate in the middle layer of the film. The films were produced on a Labtech Engineering three-layer laboratory line. Four film samples were prepared, including a reference film labelled as PE pure and made from stanard material, and films with a modified middle layer B, containing regranulate and calcium carbonate in specified proportions. The mechanical strength tests of the sealed films were conducted to verify strentght of films in aim to be used for FFS (Form-Fill-Seal) packaging lines. The PE 60 film, which includes 60% regranulate content, showed an increase in strength of hot welds (hot tack force) by 0.22N comparing to PE pure material and RPE composite films, containing 80% and 100% regranulate content, showed a decrease in hot tack force in the range of 0.87N and 1.75N respectively. Thermal properties of the samples were evaluated using differential scanning calorimetry (DSC). These measurements allowed for the determination of the melting and crystallisation temperatures of the films under investigation. The DSC results indicated that the regranulate material slightly lowers the melting temperature of the films, without significantly affecting the functional properties of the material. The spectrophotometric studies, performed for color tests of the prepared films, obtained by D65 light source settings, presents following values of ΔE* (overall color difference): 6,90; 6,19 and 6,31 for RPE 60, RPE 80 and RPE 100 respectively. In conclusion, the conducted research demonstrates that three-layer LDPE packaging films, produced with regranulate and calcium carbonate in the middle layer, retain their required mechanical and thermal properties while maintaining a consistent structure across the tested conditions, which makes them appropriate substitutes for conventional FFS films made entirely from stanard plastics for industrial applications.

Keywords: *n-layer films; blow molding; polymer composites; recycling; hot-tack*

INTRODUCTION

One of the priority branches of the plastics manufacturing is the packaging sector, which accounts for about 40% of the global demand for these materials. However, due to the short life cycle of packaging, it is the cause of about 60% of the total amount of collected post-consumer

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waste plastics, which is a important task for people and the environment, that’s why it’s necessary to develop and implement a strategy for designing and producing packaging in a way that ensures their high recyclability and the maximum use of post-production plastics or natural products in their production [1, 2]. As described in Trevor Zink's work [3], the main environmental advantage of recycling or reusing various products and materials is usually the possibility of replacing the production of primary materials. The lack of such replacement significantly limits the environmental benefits resulting from these practices. Since 2022 regulation in platic sector, especially in packaging is to reduce the negative impact of packaging and packaging waste on the natural environment [4]. According to the project's assumptions, by 2030 all packaging used in the EU is to be recyclable, and the use of recovered plastics in packaging is to be increased enough to reach the recycling rate of 55% [5-7].

In the face of growing challenges related to environmental protection, society is facing increasing demands for sustainable development. One of the key areas that require special attention is the issue of waste management, especially in the context of plastic waste. In this regard, recycling plays an extremely important role as an element of strategies aimed at reducing the negative impact of various forms of plastics on the natural environment [8, 9]. Discovering many methods to convert plastic wastes into new products enhance the sustainability of the environment was reported by Ehsan Naderi Kalali and coworkers [10]. The problem of waste material was reported also by research groups of Kotiba Hamad and Muhammad Yasir Khalid [11, 12] respectively. That is one of reason why circlar economy is very important topic nowadays and researchers try to fing optimal way to manage polymer material resources and to find different opprotunities to convert waste material into new products, including additive manufacturing, as it was reported by Vigneshwaran Shanmugam and coworkers in the work Polymer Recycling in Additive Manufacturing: an Opportunity for the Circular Economy [13]. Important role to play in promoting sustainability as part of a circular economy was presented in [14]. The important role of circular economy is reported worldwide in many works [15-17], thus due to such high demand, searching for new possibilities of managing waste material in polymer processing sectors, such as blow molding [18, 19], injection molding [20,21] or extrusion [22]. One of branches of polymer processing, where circular economy is implemented is blow molding process. This specific process gives possibility to obtain thin films

Plastic waste in form of regranulates contains a mixture of various polymers and impurities such as soil, sand, metals, paper and others, therefore, the intention set in the work is to examine the effect of regranulates on the structure and mechanical and functional properties of the film, as well as to develop optimal recipes that will ensure high product quality and repeatability of technical parameters required on automated FFS (Form-Fill-Seal) packaging lines. The search for the optimal mixture containing regranulate should be considered in a very individual approach.

The research presented in the article focuses on the analysis of the structure and properties of 3-layer composite films produced using blow molding technology [23]. To achieve better control on material feeding and ratio of materials additional support is used as precise gravimetric dosing system [24]. In order to assess the effect of the addition of regranulate and mineral filler on the properties of the film, a series of tests and studies were conducted, including spectrophotometric studies, DSC and hot-tack test (hot weld strength test). Spectrohotometry was used in connection with the fact that color of packaging films plays a key role in the marketing context and is an integral part of the branding strategy of packaging manufacturers. Color, as the first noticeable attribute of the product, affects the perception of quality and aesthetics of the packaging, which can determine the commercial success of a given product and, as has been proven, affects consumer satisfaction and even loyalty. The right choice of color very often ensures visual consistency of the brand and the products it offers, which is very important for maintaining a positive image of the company/manufacturer. The hot tackforce is measured to determine the maximum force required to break or peel a seal. This procedure allows for the evaluation of the properties of packaging materials, which is important for assessing their suitability for automated packaging processes and maintaining package integrity during storage and transportation. In addition, the analyses carried out aim to provide detailed data on the possibilities of replacing primary polymers with secondary materials, while maintaining the functionality and durability of packaging, which will certainly contribute to the implementation of sustainable development strategies and a circular economy. Concerning mentioned aibilities of application of multilayered polymer films and their impact for circular economy, especially with use of recycled materials, comparison of stanard and recycled polyethylene 3-layered films has been done and presented in this paper.

EXPERIMENTAL

The films from the developed recipes from the individual stages were prepared using the free blowing method on a 3-layer laboratory line Labtech Engineering Co., Ltd. Model LF-250 with a screw diameter of 20 mm and a L/d ratio of 30.

The temperature parameters of the individual zones were as follows (table 1).

Table 1. *Temperature profile of heating zones used in the experiment*

zone	First zone	Second zone	Third zone	Connector with the head	Head
temperature	185°C	190°C	195°C	200°C	200°C

Material was chosen according to industrial regulations, so the manufacturing of the films was focused on use of stanard thermoplastic, recycled thermoplastic and filler as particles of $CaCO_3$. Basing on these materials experimental plan was prepared to obtain different films (table 2).

Table 2. *Experimental plan – samples with filler, stanard and recycled polymer according to industrial regulations*

Sample designation	regranulate RPE	filler $CaCO_3$	granulate LDPE	Total percentage
PE pure	0%wt	0% wt	100% wt	100% wt
RPE 60	60% wt	20% wt	20% wt	100% wt
RPE 80	80% wt	10% wt	10% wt	100% wt
RPE pure	100% wt	0% wt	0% wt	100% wt

Differential scanning calorimetry (DSC) was used to investigate the differences between stanard PE (reference material) and recycled PE in aim to see processability of materials and to design experimental plan. The study was carried out using a NETZSCH DSC 214 Polyma device. The analysis was performed in the temperature range from -55 to 210°C, with a heating rate of 10.0 K/min. The NETZSCH Proteus software was used for data analysis.

The spectrophotometric studies were performed for color tests of the prepared films. Test was done using a DATACOLOR 400 dual-beam d/8° spectrophotometer, where the source of illumination was pulsating xenon. The tests were performed in accordance with the PN-EN ISO/CIE 11664-1:2019-08 standard. The CIELab color space is a mathematical transformation of the CIEXYZ space; the formulas for the transformation from CIEXYZ to CIE Lab are given below (fig. 1):

$$L = 116\sqrt[3]{\frac{Y}{Y_0}} - 16 \quad (1)$$

$$a = 500\left(\sqrt[3]{\frac{X}{X_0}} - \sqrt[3]{\frac{Y}{Y_0}}\right) \quad (2)$$

$$b = 200\left(\sqrt[3]{\frac{Y}{Y_0}} - \sqrt[3]{\frac{Z}{Z_0}}\right) \quad (3)$$

where:
X_0 =94.81
Y_0 =100.00
Z_0 =107.30
are the coordinates of the color of a nominally white body. The difference between two colors in the CIE Lab space takes the form:

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

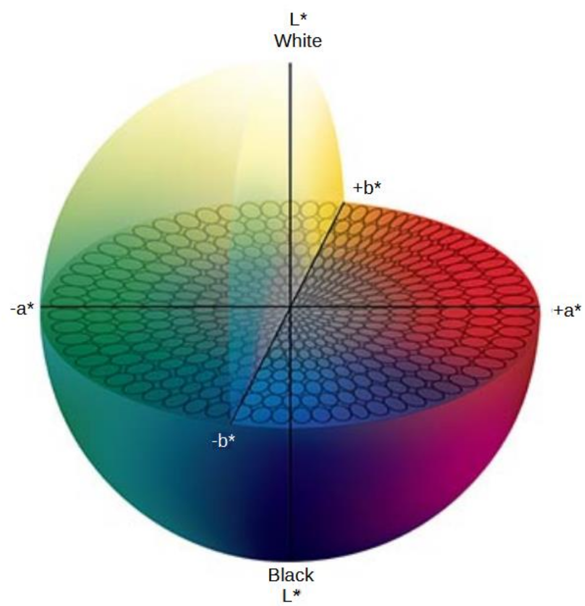

Fig. 1. CIELab color space

ΔE^* is the Euclidean distance between two points in three-dimensional space. The study was conducted for different light source settings (D65, A, F02) with an observation angle of 10 degrees. D65 simulates daylight, A refers to incandescent light, and F02 to fluorescent light. Different light sources have different spectra, which can significantly affect color perception. The 10-degree observation angle is an industry standard that takes into account common color observation conditions while ensuring consistency and comparability of results.

The tests of strength of hot welds were carried out using the PARAM HTT-L1 hot tacktester from Labthink, in accordance to the ASTM F1921 standard, which is commonly used to measure the strength of thermal welds between flexible tapes with thermoplastic surfaces. In the test a rectangular sample is fixed in a holder of the testing device, while the other end of the sample is connected to a holder with an actuator. Then the film is precisely placed between the sealing rods using a sample positioning mechanism as lap joint and subjected to stretching with crosshead speed of 1500 mm/min (fig. 2). A minimum of 10 samples were tested in each series to ensure statistically significant and reliable results.

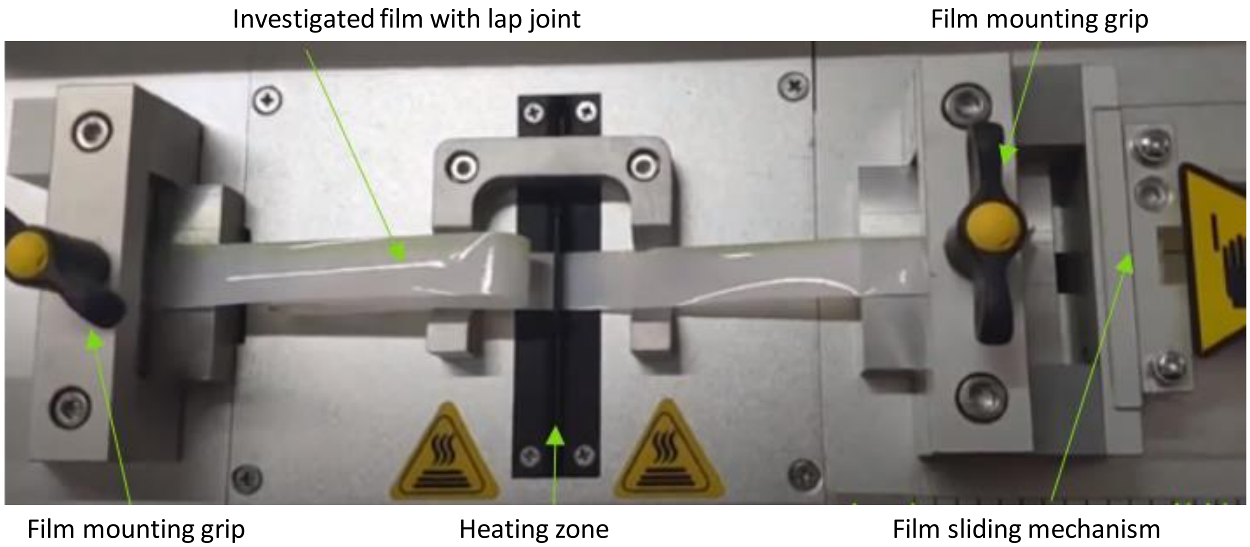

Fig. 2. Sample mounting in the PARAM HTT-L1 Hot tack device

RESULTS AND DISCUSSION

The differences in the recorded spectra of the stanard granulate and the regranulate (fig. 3) may result from the thermal-mechanical processes occurring during recycling, which affect the microstructure of the polymer. These processes may lead to changes in the distribution of crystallites and the amorphous phase. In addition, these differences may also be the result of using a blend of LDPE and LLDPE (Linear Low-Density Polyethylene) materials for the production of regranulates. This material has more linear structure than LDPE, while having a similar density, and the range of temperatures for sealing is 118-125°C [26]. The literature shows also wider hot tack window of sealing temperature for these polyolephins ranging between 110 and 140°C [27]. The most suitable temperature chosen for investigated materials was closer to maximum temperature, that is 135°C. It may be due to multilayer structure of the film. Despite these differences, the results indicate that the PE regranulate retains thermal properties similar to the stanard LDPE granulate, which makes it a suitable material for use as a modifier for FFS films, providing thermal stability and appropriate mechanical properties.

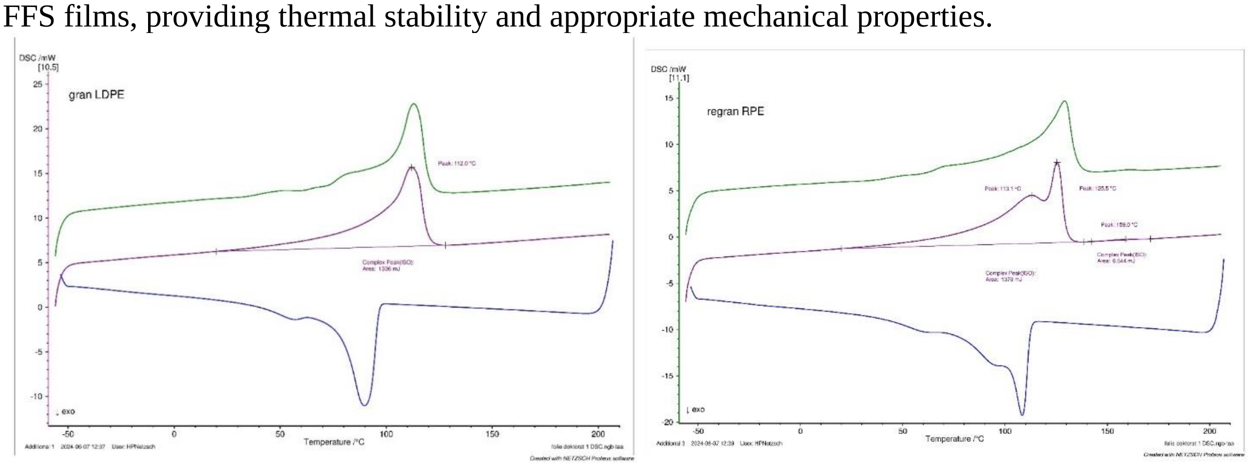

Fig. 3. DSC curve for the stanard LDPE granulate (left) and for the regranulate RPE100 (right) obtained during thermal analysis

In order to verify the degree of color change of the film containing modifiers, in relation to the color of the reference film, the acceptance criterion for the ΔE* was verified in spectrophotometric test. All samples were tested for different light source settings (D65, A, F02). The results are presented in the table 3 and fig. 4 below.

Table 3. *Results of the evaluation of color differences of films, carried out using D65 standard at an observation angle of 10°, A standard at an observation angle of 10° and F02 standard at an observation angle of 10°*

Sample	ΔE*			ΔL*			Δa*			Δb*			ΔC*			ΔH*		
PE pure	Reference sample																	
Light source	D65 10°	A 10°	F02 10°	D65 10°	A 10°	F02 10°	D65 10°	A 10°	F02 10°	D65 10°	A 10°	F02 10°	D65 10°	A 10°	F02 10°	D65 10°	A 10°	F02 10°
RPE 60	6.90	6.98	7.08	-6.03	-5.73	-5.84	0.66	1.34	0.33	3.29	3.75	3.99	3.35	3.97	3.99	0.15	0.24	0.25
RPE 80	6.19	6.22	6.35	-5.55	-5.32	-5.40	0.40	0.97	0.16	2.72	3.08	3.34	2.75	3.21	3.33	-0.05	0.28	0.28
RPE pure	6.31	6.32	6.46	-5.71	-5.49	-5.56	0.27	0.84	0.07	2.69	3.01	3.29	2.70	3.11	3.28	0.01	0.33	0.32

The results of spectrophotometric tests confirm the differences in lightness, saturation and hue, which may be important for quality control in the production process. Particularly high values of the ΔE* index indicate a significant color difference between the modified and reference films. Differences in Δa* and Δb* values indicate chromatic changes in the samples compared to the reference. The observed negative ΔL* values suggest that the samples are darker. Positive Δa* and Δb* values indicate an increase in color saturation and a color shift towards red (Δa*) and yellow (Δb*).

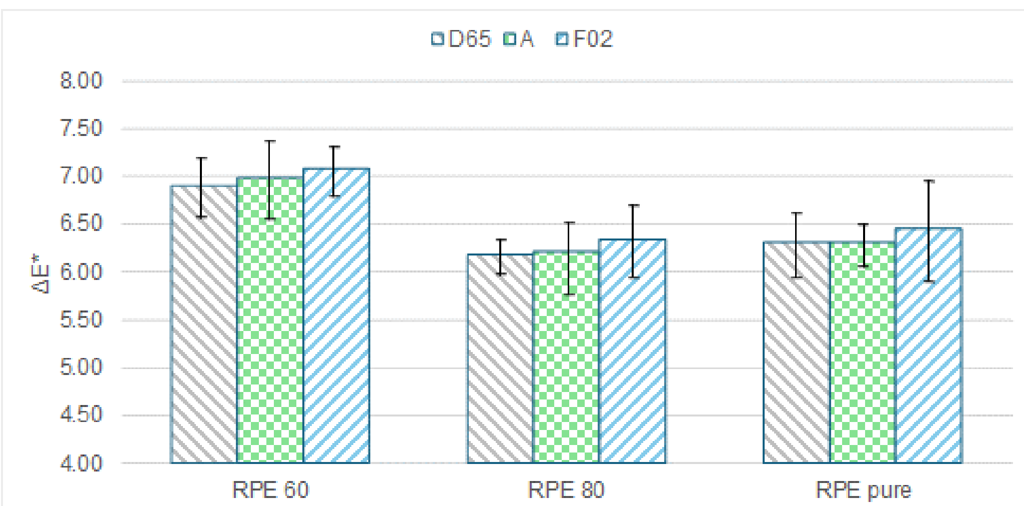

Fig. 4. Comparison of ΔE* (overall color difference) values for different modified films under different illumination standards: D65, A, and F02 at 10° viewing angle. Values represent color changes compared to the PE pure reference film

The color tests of the samples showed that all modified film RPE 60 is characterized by a significant color difference compared to the reference film PE pure, which is confirmed by high values of the ΔE* parameter, exceeding the acceptability threshold. Reflectance and opacity tests confirmed that the modified films are characterized by a lower degree of light reflection and higher opacity than the reference film, which also affects their color perception. Despite exceeding the acceptable color differences, these changes can be beneficial, emphasizing the ecological nature of recycled packaging [9].

In order to select the optimal SIT sealing temperature for weld break force test, all films were tested in a wide temperature range, starting from 110°C, which is the average melting temperature for polyethylene, and ending at 140°C, where the sealing joint burned through. In the test was chosen temperature of 135°C.

Table 4. *Average weld break force results at weld temperature 135°C*

Sample	Average break force	Standard deviation
	N	N
PE pure	4.95	0.94
RPE 60	5.17 ↑	0.3
RPE 80	4.08 ↓	0.73
RPE pure	3.20 ↓	0.68

The tested films can be divided into two types – the one which achieved higher hot tackforce values compared to the value measured for the reference film and those that achieved lower values. The first type includes film with 60% regranulate content, which showed an increase in hot tack force by 0.22N. The second group includes films with 80% and 100% regranulate content, which showed a decrease in hot tackforce in the range of 0.87N and 1.75N respectively. However, it should be noted that the recorded decreases of Hot Tack values do not disqualify the indicated films in terms of their application on packaging. During the test of welded joints at 135°C, it was confirmed that the welds of all samples maintained their integrity during stretching (Fig. 5). Further examination of structure after test is indicated to understand adhesion and possible defects, as it is presented in [28].

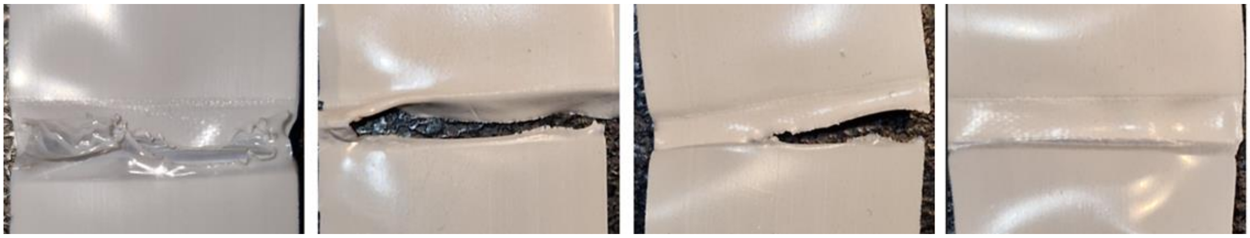

Fig. 5. Welds of film samples after Hot tacktesting, from the left: RE pure, RPE 60, RPE 80, RPE pure

The welded samples showed high strength, with improved weld strength for selected samples. The best results were obtained for RPE 60 comparing to reference sample, however observation of RPE pure sample gives expectation for improving properties with appropriate selection of technological parameters.

CONCLUSIONS

The effect of material composition on properties of obtained film composites is reported in this work. Four film samples were compared including fully stanard and fully recyclated materials and middle condition materials with samples containing different ratio of recyclate and filler. Performed experimnets and obtained results formulate the following conclusions:

- DSC test reveals that the RPE pure material from regranulate presents thermal properties similar to the stanard LDPE granulate, which makes it a appropriate material for use as a modifier for Form-Fill-Seal packaging lines,
- reflectance tests confirmed that the modified films affects their color perception and are categorized by a lower degree of light reflection and higher opacity than the reference film, however do not exceede the acceptable color differences,
- observation of films after strength of hot welds tests of RPE pure sample gives expectation for improving properties with appropriate selection of technological parameters.
- the PE 60 film, which includes 60% regranulate content, showed an increase in strength of hot welds (hot tack force) by 0.22N comparing to PE pure material. The RPE composite films, containing 80% and 100% regranulate content, showed a decrease in hot tack force in the range of 0.87N and 1.75N respectively, however, these values do not disqualify the indicated films in terms of their application on packaging.

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