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Multilayer Flexible Packaging Materials: Relationship between Structure and Functional Properties

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FLEXIBLE packaging material is one of the huge sectors in packaging industries which feed wide range of industries etc. food, medical, beverage and other daily used products. Different structures of flexible packaging materials and their functional properties have been discussed. Ten popular multilayer laminated structures have been evaluated. These laminates are used extensively in the flexible packaging sector to demand various application purposes. The evaluation of these multilayer structures was conducted by assessment of barrier properties, mechanical properties and overall migration rates. The barrier properties were investigated by measurement of water vapor and oxygen permeability. The mechanical properties were studied through measurement the tensile strength and elongation at break %. The overall migration was tested for all samples according to EU Regulation Nr. 10/2011. The different structures showed highly satisfied functional properties that needed for each application.

Keywords: Flexible packaging, Lamination, Permeability, Migration, Mechanical properties.

Introduction

Flexible packaging is considered as one of the most important industries for our daily life. That is due to its fulfillment the requirements for various applications (i.e. food, cosmetics, medical, detergent, etc.). The flexible packages should have many functions such as protection during product's shelf life, containing and decorative purposes [1-7]. This packaging technique can meet several advantages such as light weight, toughness and flexibility. The higher barrier properties such as metal or glass are still challengeable for flexible packaging. For that, in many cases mono-layer package is not enough for numerous applications. That induces the increase in the demands for multilayer laminated structures (MLLS) [8,9]. MLLS are normally composed of outer layer, back printing, adhesive and inner layer. The printing process can be printed *via* different techniques such as flexography or rotogravure printing. The lamination process has sundry types such as wet, dry, wax, solventless and extrusion. This process can lower the cost by reducing the expensive packaging layers with keeping the desired performance. Different structures for laminated layers had been designed (i.e. OPP/OPP, PET/PE, PET/Alu/PE, etc.). Many improvements are going to fulfill the significant rates for the emerging new packaging applications. The properties can be improved by lamination process such as barrier to water vapor and different gases (oxygen, nitrogen and carbon dioxide), light protection, aroma preservation, toleration of various filling conditions, sealing, mechanical, chemical and thermal resistance. The plastic film itself can be improved through several processes. The processes are such as metallization, matting, pigmentation, etc. The metallization process is a decorative coating for plastics and papers that can be achieved by vaporizing of the molten metal on the substrate to be coated under vacuum condition [8]. This can impart the substrates various properties such as barrier, light protection and security. More than 65 % of the metalized films are used in flexible packaging sector. The metalized substrates

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are mainly oriented polypropylene (OPP) and polyethylene terephthalate (PET) [10]. Also matting and pigmentation the packaging substrates are used for functional and decorative purposes. In this work ten popular laminated structures have been studied. In this research field the academic publications are few and that encourage us for more academic study. The study covers the correlation between the different structures and various properties such as mechanical, barrier (i.e. water vapor, oxygen) and the overall migration levels in different simulants.

Materials and Methods

Materials

Ten multi layers laminated were supplied by Rotographia company, Cairo, Egypt. The laminated structures were chosen carefully to cover many applications in the Egyptian market. MLLS are mainly based on back printed OPP (transparent or matt) and PET laminated with various substrates such as OPP, metalized cast polypropylene (MCPP), metalizedoriented polypropylene (MOPP), white cast polypropylene (WCPP), white metalizedoriented polypropylene (WMOPP), transparent polyethylene (PE), white polyethylene (WPE) and aluminum (Alu). The thicknesses of the laminated layers are presented in Table 1. The printing process was conducted by rotogravure printing method using solvent based inks. The lamination process was achieved using polyurethane adhesives. The duplex structures were laminated using general performance solvent less adhesive. The triplex structures were laminated using high performance solvent-based adhesive.

Methods

Water vapor and oxygen permeability

Water vapor transmission rate (WVTR) was carried out using GBI W303 (B) Water Vapor Permeability Analyzer (China) using the cup method. WVTR was measured as the mass of water vapor transmitted throughout a unit area in a unit time under controlled conditions of temperature (38^{o}C) and humidity (4%) [11]. Also, the oxygen transmission rate (GTR) was measured by N530 Gas Permeability Analyzer (China) [12].

Polarization optical microscopy (POM):

The topographic texture of laminated flexible packaging films was investigated using Leica DM750P polarizing optical microscope (Leica Microsystem GmbH, Switzerland). The crossed polarizers plus 530 nm filters were employed for measuring the morphology of the surfaces. All measurements used Leica 4X, 10X and 20X long working distances lens.

Tensile strength and elongation

Mechanical properties of laminated flexible packaging films; tensile strength (TS), and elongation at break (E) of films were measured by Zwick/RoellZ020 instrument, (Ulm, Germany) [13].

Overall migration tests

The overall migration (OM) for laminated structure samples in different simulants was occurred according to EU Regulation Nr. 10/2011. Simulant A: 10 % v/v ethanol, Simulant B: 20 % v/v ethanol, Simulant D2: rectified olive oil. All laminated films were measured in relative to blank sample (Millipore water with resistivity 18.5 MΩ) as reference. The OM is presented as the milligrams of migrated material from one decimeter square surface (mg/dm^2). The laminated samples are printed, for that one side as the side cell method was used as the simulant conditions for packing item. The results were calculated corresponding to the area of only one surface of the test specimen. After incubation in weather simulating chamber for 10 days at 40 °C, the samples were removed and dried over

TABLE 1. The thicknesses of different laminated structures.

Structures	Thickness, µm	The overall thickness, µm
OPP/OPP	20/20	50
OPP/MCPP	25/25	60
OPP/MOPP	20/20	50
OPP/WCPP	20/30	60
MattOPP/MOPP	20/30	70
MattOPP/Alu/PE	20/6.35/50	90
PET/Alu /PE	10/6.35/30	65
PET/WMOPP	12/30	50
PET/PE	12/110	130
PET/WPE	12/30	50

rotatory evaporated at 90 °C (EN 1186-5-single side contact in cell test) [14].

Results and Discussion

Water vapor and oxygen permeability

One of the important issues for using flexible packages is their ability to permeate gases, vapors. That limit its use to the products do not need highest barrier protection. That induced the market needs to keep the dry products dry and moist the product moist. Many appreciated efforts were conducted to control the barrier properties for flexible packages [15-17]. To achieve minimal barrier properties required high ability to control many factors. These factors such as polarity, fillers and blends, cross-linking, orientation, chain stiffness, crystallinity and external shielding.[18] The barrier properties were studied by investigation the water vapor and oxygen permeability for various laminated structures [19,20]. OPP and PET are used mainly for study the effect of different layers on the permeability. OPP was laminated with WCPP, OPP, MCPP, MOPP.

The highest barrier properties achieved for OPP by laminating with MOPP. The highly importance for the orientation of the molecular chains that due to the increase in the degree of crystallinity [9]. The metallization process also offered an improvement in the barrier properties as shown in Table 2. In contrast to the effect of white pigmentation and the absence of an orientation of the plastic films that leading to significance decrease in the barrier properties. The matting effect also showed increase in the barrier properties by three-folds than the transparent glossy one. Although, it is well known the outstanding properties of PET such as tear resistance, high transparency, gloss and highly resistance to scratching and abrasion. PET can achieve these highly desired properties even at low thickness (i.e. 12 µm). Also, low barrier properties were observed with WPE laminated film. The decrease in barrier properties accompanied for lamination with white films (i.e. WCPP, WPE) is mainly due to the presence of titanium dioxide pigment and different fillers. The triplex structures (Mattopp/Alu/PE and PET/Alu/PE) were showed high barrier properties due to presence of Alu substrate. Presence of pinholes was the main reason for non-zero permeability properties.

Investigation of the laminates by polarized optical microscope

The good appearance of the flexible packages is important for customer evaluation of the product. The apperance is checked by simple visual observation. There are many apperance troubles can be effected on the visual quality of the product specially in white and yellow printing areas. These troubles such as spots, poor clarity, orange peel, ghosting, lines with different colors and misregestration. The formation of sposts has many reasons such as formation of CO_2, insufficient grinding of the pigments, poor treatment of the substrates and trapped air.

The formation of CO_2 is due to reaction of unreacted isosynate monomer, from PU adhesive, with water from the surrounding air which leading to amine formation and CO_2 as shown in scheme 1. This trouble specifically is related to the permeability of the substrates. It was appeared frequently in the multi layers structurs which have high barrier properties (i.e. PET, MOPP, Al, NY, PVDC coated films). This may be attributed to trapping of the formed CO_2 gas and its disability to permeate through the laminated substrates. The

TABLE 2. Water vapor and oxygen permeability for various laminates.

Sample	O_2TR, cc/(m^2.24h)	WVTR, g/(m^2.24h)
OPP20/WCPP30	944.00	3.43
OPP20/OPP20	529.30	1.67
OPP25/MCPP25	148.80	1.27
OPP20/MOPP20	67.50	0.52
MattOPP20/MOPP30	18.60	4.12
MattOPP20/Alu6.35/PE50	0.04	0.03
PET12/WPE30	95.40	10.90
PET12/PE110	87.10	2.92
PET12/WMOPP30	27.80	3.24
PET10/Alu 6.35/PE30	0.015	0.01

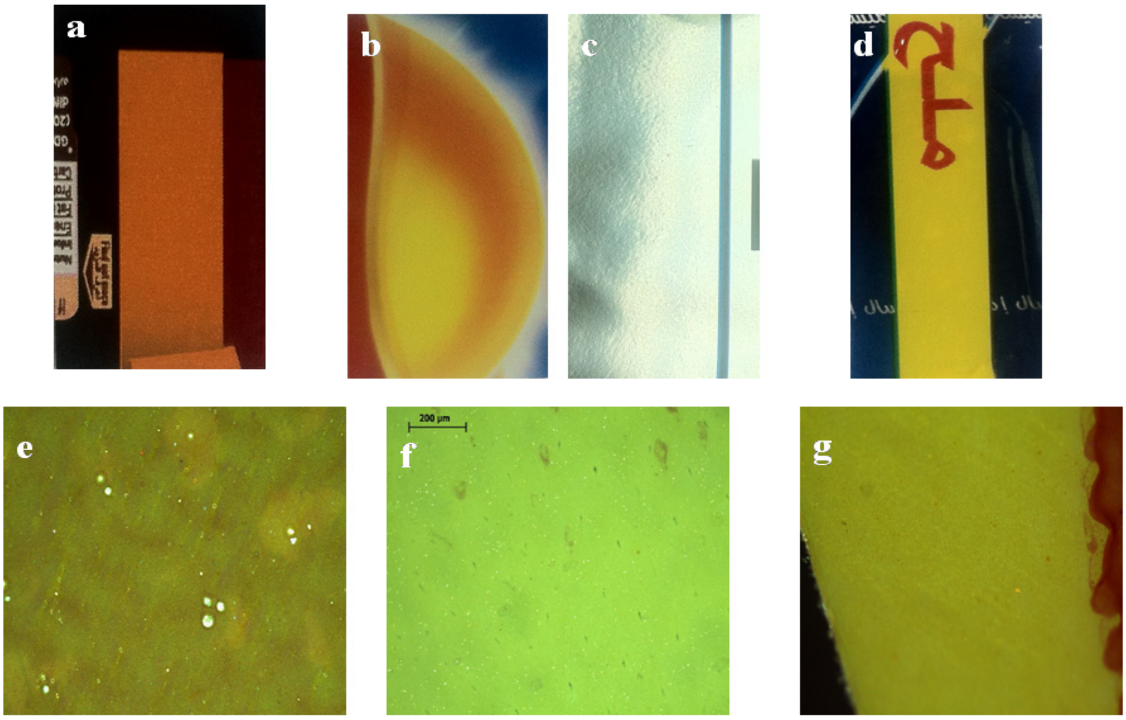
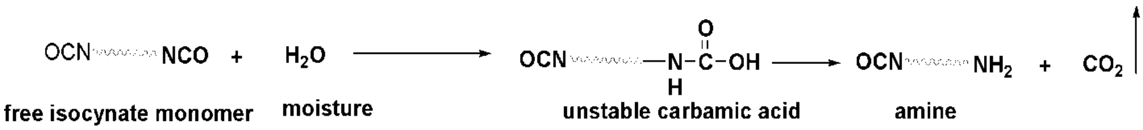


Fig. 1. The investigation of various laminates by using polarized optical microscope.



Scheme 1. The formation of CO_2 during curing process.

apperance of different laminates structures was checked by using polarized optical microscope (Fig. 1) [21,22]. It was shown clearly observation of trapped CO_2 spots in high barrier laminated structures which contains PET/Alu/PE (Fig. 1a,e) and OPP/MOPP (Fig. 1b, f). The clear absence of trapped CO_2 was observed in case of low barrier substrates (Fig. 1d,g). Some processing solution was tried to improve the laminates apperance by increasing the adhesive coating weight that can lead to another apperance problems such as orange peel (Fig. 1c).

The mechanical properties.

The evaluation of mechanical properties for the laminated structures was conducted by measurement of tensile strength (TS) and elongation at break % (E %). Many parameters should be taken into consideration to achieve the desired mechanical properties that meet the application demands. These parameters such as substrate types and its orientation, thickness of the substrate and the different types of modifications (i.e. white pigmentation, metalizing, matting,…). The tensile strength and elongation at break % were measured in machine and transverse directions.

The effect of orientation for the molecular chains was clearly observed by lamination of OPP with MCPP or MOPP. The TS and E % are higher in case of MCPP than others laminated films. In addition, TS and E % get higher in machine direction than in transverse direction. The lamination with white pigmented substrates WCPP, WPE and WMOPP had weakened the mechanical properties. It was observed also the convenient of the structure design and the proposed product that will be filled regarding weight.

TABLE 3. The mechanical properties of the multi layers structures

Product's weight, g	Purposed application	Elongation at break %	Tensile strength, MPa	Samples
50	Bakery	100.40	61.30	OPP25/MCPP25, MD[a]
		26.10	78.90	TD[b]
58	Fried potato	64.50	56.20	OPP20/MOPP20, MD
		26.40	54.40	TD
Blank		35.20	50.10	OPP20/OPP20, MD
		42.60	48.80	TD
125	Soap	61.60	34.60	OPP20/WCPP30, MD
		NA	NA	TD
50	Fried crackers	76.40	52.10	MattOPP20/MOPP30, MD
		41.80	66.50	TD
36	Snacks	81.40	36.50	MattOPP20/Alu6.35/PE50, MD
		14.30	51.10	TD
18	Coffee	37.15	58.90	PET10/Alu 6.35/PE30, MD
		39.17	55.10	TD
500	Table salt	30.50	27.15	PET12/WPE30, MD
		17.25	19.60	TD
5000	Rice	343.70	27.00	PET12/PE110, MD[c]
		45.25	32.77	TD
28	Biscuit	25.30	24.20	PET12/WMOPP30, MD
		8.30	56.60	TD

[a]MD: machine direction, [b]TD: transverse direction, [c]The PET layer tear and the polyethylene layer elongated

The overall migration

Many international authorities had set regulations regarding migration of specific chemicals from packaging materials. These migrated low molecular weight substances such as degradation products, additives, monomers and catalysts. These migrated substances could have bad taste, odors or suspected harmful effects to humans [23-25]. These chemicals diffused and desorped from the packaging materials. Then consequently sorped at plastic-food interface and desorped to the food. The overall migration was conducted according to EU Regulation Nr. 10/2011. In this regulation food types and food simulants had been classified to nine types recommended by FDA to simulate the effect of different food types such as aqueous, acidic, fatty, etc. The accepted limit for the overall migrated substances according to the regulation is 10 mg/dm^2 or 60 mg/kg in the food. According to this regulation, the studied multi layers laminated structures were tested to determine the overall migrated chemicals by using gravimetric method. The migration tests were conducted using three simulants to represent variety of expected food types. The simulants were 10% v/v ethanol, 3% w/v acetic acid and olive oil. Table 4 shows that the overall migration limits for the studied structures are in the accepted levels according to EU Regulation Nr. 10/2011. It is worth to mention that, the white pigmented plastic films such as WCPP and WPE have higher migration rates than other substrates. This may be due to presence of fillers and pigments that increase the possibility for low molecular weight substances to migrate. But in case of metallization the white films the migration levels were lowered.

Conclusions

In this article we studied ten different multi layers laminated structures. These structures were chosen due to their commonly used as flexible packages. The oxygen and water vapor permeability were measured to evaluate the barrier properties. The film orientation, metalizing and matting were showed remarkable increase in the barrier properties, in contrast to white pigmentation and absence of orientation. The

TABLE 4. Overall migration results for the studied laminated structures

Sample	Migration into 10% v/v ethanol (simulant A) mg/dm²	Migration into 3% w/v acetic acid (simulant B) mg/dm²	Migration into Olive oil (simulant D_2) mg/dm²
OPP20/WCPP30	4.0	5.0	1.5
OPP20/OPP20	2.0	3.0	0.7
OPP25/MCPP25	0.8	0.9	0.4
OPP20/MOPP20	0.1	0.2	0.1
MattOPP20/MOPP30	0.2	0.1	0.0
MattOPP20/Alu6.35/PE50	1.7	2.3	0.7
PET12/WPE30	6.0	7.0	3.0
PET12/PE110	1.3	1.6	0.6
PET12/WMOPP30	1.0	2.0	0.9
PET10/Alu 6.35/PE30	1.9	2.1	0.6

tensile strength and elongation at break % showed highly convenient of the desired mechanical properties and the proposed application. The overall migrations were in the accepted levels according to EU Regulation Nr. 10/2011.

Declarations of interest: none

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مواد التعبئة والتغليف المرن متعددة الطبقات: العلاقة بين التركيب و الخواص الوظيفية

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يعتبر قطاع التغليف المرن من القطاعات الضخمة التى تغذى صناعات عدة مثل صناعة الغذاء، الدواء، المشروبات و منتجات كثيرة للأستخدام اليومي. في هذا البحث تم مناقشة تركيبات مختلفة لمواد التغليف المرن وخصائصها الوظيفية. تم تقييم عشر تركيبات مبطنة مختلفة. التقييم تم بإختبار خواص النفاذية، الميكانيكة و معدلات الهجرة الكلية. خواص الحجز تم دراستها بقياس نفازية بخار الماء والأكسجين. وتم دراسة الخواص الميكانيكية بقياس قوة الشد و نسبة الأستطالة. وتمت دراسة الهجرة الكلية للمركبات من مواد التعبئة والتغليف طبقا للمواصفة الأوربية ٢٠١١/١٠. وأظهرت التركيبات المختلفة ملائمة كبيرة للخواص الوظيفية للتطبيقات المختلفة.