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Advanced aesthetic material solutions for car interiors

Madalin Parvu
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Advanced aesthetic material solutions for car interiors

By

Madalin Parvu

A Thesis

Submitted to the Faculty of Graduate Studies
through the Department of Mechanical, Automotive and Materials Engineering
in Partial Fulfillment of the Requirements for
the Degree of Master of Applied Science
at the University of Windsor

Windsor, Ontario, Canada

2018

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Declaration of Originality

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Abstract

The current study is focused on the identification of the factors that influence the soiling propensity of the polymeric materials adopted in the passenger compartment over eleven different textures. The polymers under analysis are different formulations of polypropylene, thermoplastic polyolefin and polyamide, in dark and light color. The results of the soiling tests have been correlated to the surface energy, the surface hardness and flexural modulus. Furthermore, being a novel field of work the definition of suitable test methodologies is addressed as well. Three test methodologies have been developed starting from real life scenarios and previous available technology. They differ in the intensity of the applied load during testing and in the adopted soiling agent. The level of soiling of a surface is defined as the difference in color between the soiled and clean areas of the part evaluated according to the CIELAB scale.

Dedication

*În numele celor care au curaj și voință,
Cred în bunul simț, muncă și dorință,
Fac ce iubesc uitând de suferință
Și trec peste orice cu credință*

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List of Abbreviations

CAH	Contact angle hysteresis
CIE	Commission Internationale de l'Eclairage
EPM	Ethylene-Propylene Rubber
EPDM	Ethylene-Propylene-Diene Rubber
PA	Polyamide
PP	Polypropylene
SNR	Signal to noise ratio
TPE	Thermoplastic elastomer
TPO	Thermoplastic polyolefin
WCA	Water contact angle

List of Symbols

ϑ	Water contact angle
γ	Surface tension
ϵ_0	dielectric constant of the medium between surfaces
ν	Frequency of the light radiation
Φ	Electrostatic potential in the vacuum in the vicinity of the material
Φ_C	Contact potential
A	Hamaker constant
d_c	cylindrical particle diameter
d_p	spherical particle diameter
d	Average between the two diagonals of the indentation
e	Electron charge
E_F	Fermi level inside the material
E_g	Energy gap between valence and conduction band
h	Plank constant
HV	Vickers hardness value
P	Applied force in microhardness test
Q	Electric charge of a particle
T_g	Glass transition temperature
T_m	Crystalline melting temperature
W	Work function
$W_{i,j}$	work of adhesion of media i and j in void
Z_0	distance between the particle and the surface

1. Introduction

Nowadays the biggest concern of the automotive industry is that of reducing its footprint on the environment. There are multiple areas where car manufacturers and suppliers can act and one of this is weight reduction of the vehicles. It can be achieved by adopting more advanced manufacturing processes as well as lighter materials. Polymers adoption falls in this last category because of their light weight, low cost and possibility of recycling. Automotive passenger compartments largely adopt polymers as can be seen in Figure 1. They must meet two requirements: aesthetic appeal and mechanical integrity. Aesthetic appeal is related to customers' perception of the product which should convey a sense of quality as well as luxury. Mechanical integrity is related to the ability of the components to maintain their original shape and integrity during the vehicle lifecycle. Recent J. D. Power surveys showed that surface damage reduction and soiling prevention play an important role in achieving long term customer satisfaction. The former has been investigated in a previous project while the latter is addressed starting with the current work. Therefore, alongside with results evaluation a robust test procedure is to be identified. This thesis focuses on the resistance to soil of different compositions of thermoplastic polyolefin blends (TPOs), polypropylene impact copolymers (PP) and polyamides (PA). The aim is to evaluate the influence of the materials and of the textures on the amount of dirt on the surface.



Figure 1.Chrysler Pacifica passenger compartment, front row [1].

1.1 Thesis organization

This master thesis is organized as follows:

- Chapter 2: *Objectives and procedure*
In this chapter information about the aims of this work as well as the experimental procedures is provided.
- Chapter 3: *Literature review*
In this chapter information about self-cleaning materials adopted in other fields is provided. Then the different types of interactions that provide adhesion of particles on surfaces are introduced. At the end the characteristics of the polymers' macro-categories adopted for this work are discussed.
- Chapter 4: *Methodology*
This section contains a detailed description of the steps followed in the experimental work. It includes information about the materials, the samples preparation, and the tests and data collection.
- Chapter 5: *Results and discussion*
The collected data is reported and analyzed in this chapter. The experimental results include color difference, hardness measurements and surface energy evaluation.
- Chapter 6: *Conclusions*
In this chapter the findings of the experimental work are summarized.
- Chapter 7: *Recommendations*
In this chapter recommendations for future developments are provided.

2. Objectives and procedure

The objective of the experimental work is an investigation of the soiling prevention response of three categories of polymers with different textures: TPO, PP impact copolymer and PA, with different compositions for each one in light and dark colors. Soiling prevention is a novel field of work therefore, there were no known tests currently available. Thus the first step was to identify a test methodology close to the actual operating conditions of the polymers in the passenger compartment. After careful considerations three tests were identified. The second step was to identify the materials to be used and specimens with different compositions which belong to three most adopted macro-categories of polymers were selected. Then a test plan was developed and soiling and surface hardness of the polymers were measured; furthermore, surface energy was evaluated from the contact angle between a droplet of water and the surfaces of the polymers. Soiling was evaluated as a difference in color between the clean and the soiled areas of the specimens. A portable spectrophotometer was used for this measurement.

3. Literature review

In this section an overview of the self-cleaning surfaces is provided. Then the factors influencing the adhesion of particles to surfaces are described. At the end a review on the polyolefin based thermoplastics and their application is provided.

3.1 Self-Cleaning Surfaces

Self-cleaning technology development started in the late 20th century based on examples from living nature, as can be seen in Figure 2, in order to reduce maintenance cost, use of detergents and effort [2]. Self-cleaning capability of a surface can be obtained by means of superhydrophobic/philic surfaces.

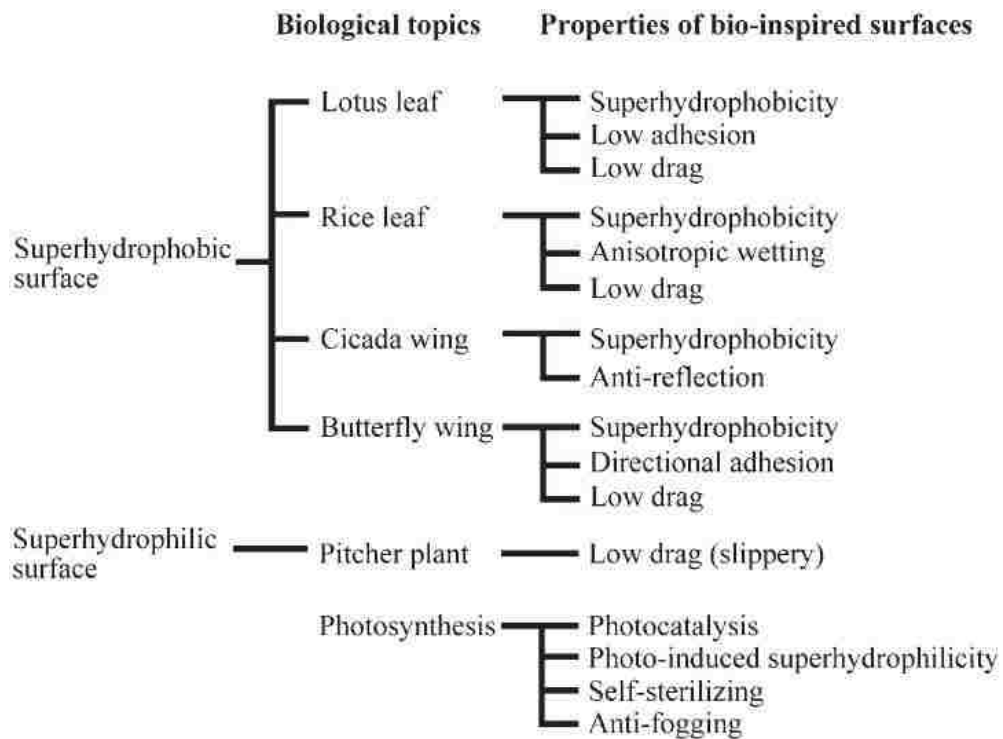


Figure 2. Overview of the self-cleaning surfaces inspired by nature [2].

3.1.1 Wettability

Superhydrophobic and superhydrophilic self-cleaning surfaces need the presence of water therefore, it is important to know what their wettability is. The latter can be assessed by measuring the water contact angle WCA, the angle θ between the tangent to the liquid-air interface and the tangent to the solid-air interface [3].

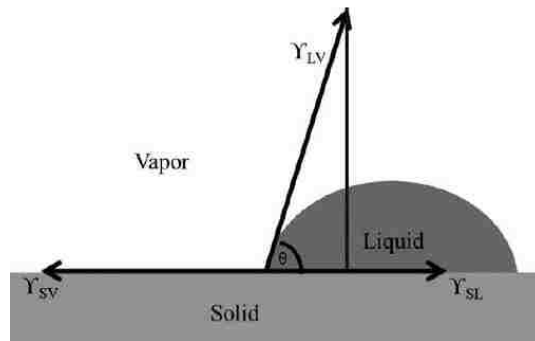


Figure 3. Contact angle measurement [3].

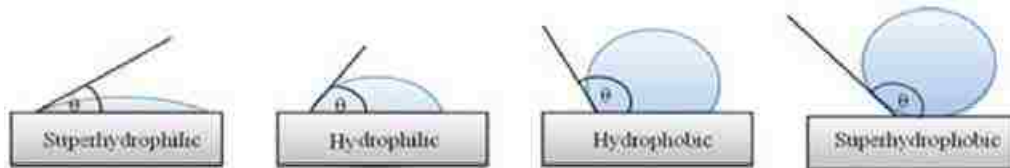


Figure 4. Contact angle examples [3].

The contact angle depends on the surface energy, surface roughness and surface cleanliness [4]. Surfaces with WCA lower than 90° are hydrophilic while those with WCA higher than 90° are hydrophobic. For each category a further distinction can be made by introducing superhydrophilic and superhydrophobic surfaces. Their WCA are lower than 10° and higher than 150° respectively [5][3][2]. High surface energy and polar

molecules on the surface lead to hydrophilicity while low surface energy and non-polar ones leads to hydrophobicity [4].

Contaminant removal working principle is similar, yet as can be seen in Figure 5, on a superhydrophobic surface water droplets roll off and carry the contaminants that stick to it while on a superhydrophilic surface, water goes beneath the contaminants and carries them away.

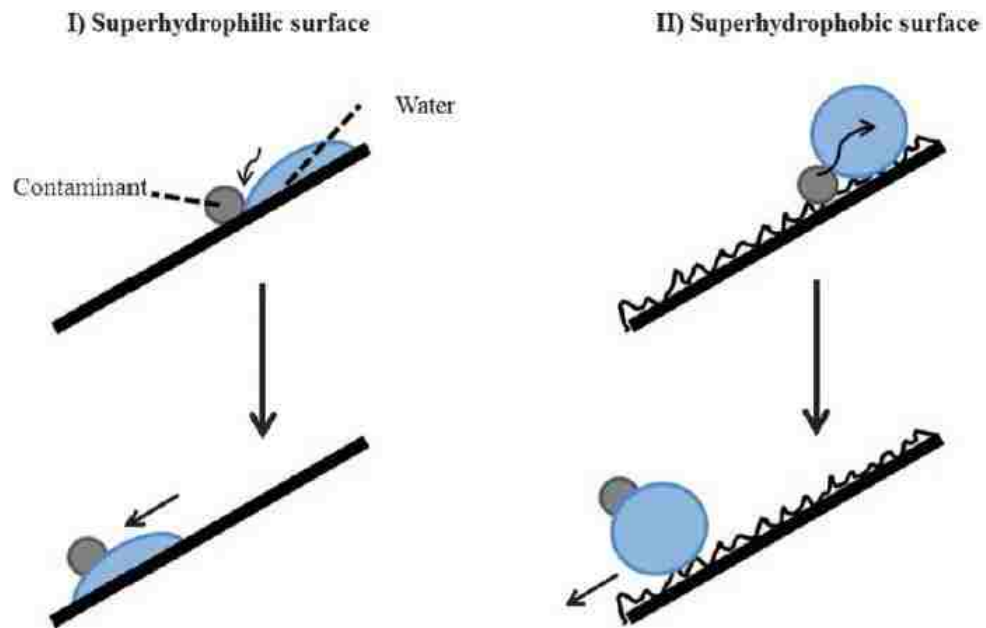


Figure 5. Self cleaning processes illustration [3].

3.1.2 Superhydrophobic surfaces

Superhydrophobic surfaces are water repellent and this allows water droplets to roll off once the surface is tilted by a given angle called tilting angle. Usually the latter should be lower than 10° for a self-cleaning surface [4][2][3][5]. Another important parameter used to evaluate the ability of a droplet to roll off is the contact angle hysteresis CAH. It is related to the irreversibility of the wetting/dewetting cycle, therefore to the energy dissipation during the flow, and it is measured as the difference between the contact angle at the front and at the back of the droplet. Contact angle hysteresis depends on surface roughness and heterogeneity.

One way to enhance hydrophobic behavior of a surface is to change its roughness. In order to obtain superhydrophobic surfaces a hierarchical roughness is required. It features a nanostructure on top a microstructure and it is effective because the higher asperities are not permeated by the capillary waves while the lower ones prevent nano droplets from filling the gaps between the former [4].

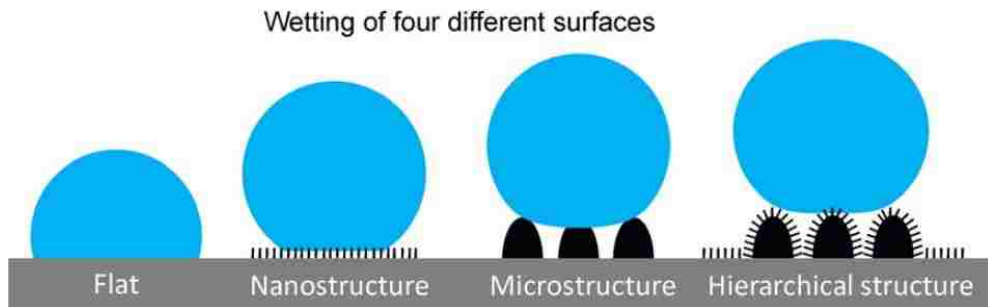


Figure 6.Wetting of four different surfaces [4].

3.1.3 Self-cleaning surfaces examples

Self-cleaning surfaces design was inspired by living nature and now there is a wide range of applications such as:

- Moon mission of exploration equipment [6]
- Solar panels [7]
- Self-cleaning windows and windshields [2][8]
- Exterior paints for buildings [2]
- Roof tiles [4][9][2]

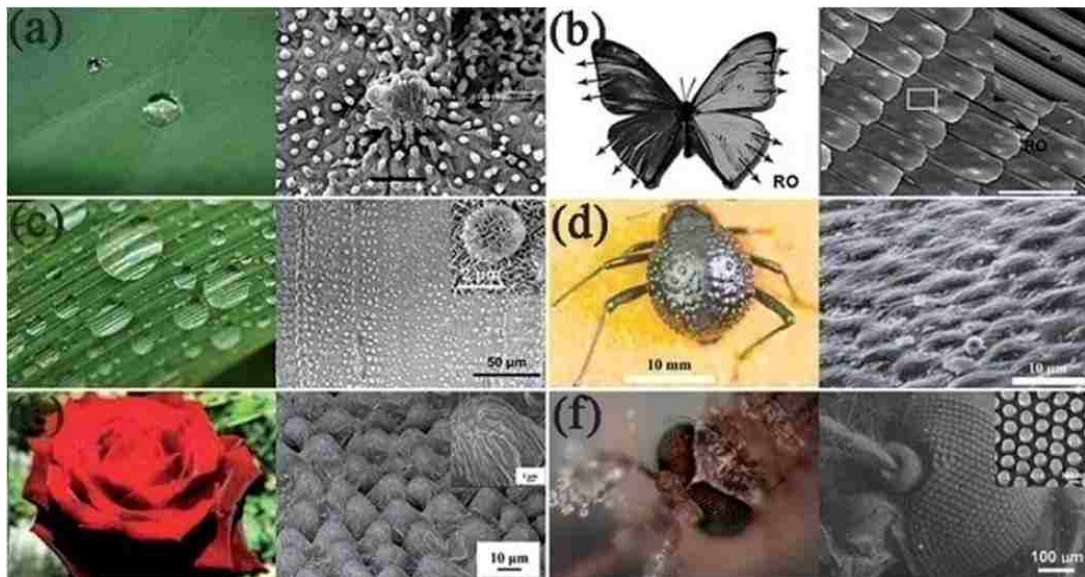


Figure 7. Mimicking nature, Superhydrophobic surfaces: a) lotus leaf, b) butterfly wing, c) rice leaf, d) desert beetle, e) rose petals, f) mosquito eyes [9].

3.1.4 Lotus Flower

Lotus flowers grow in ponds and despite expectations are always clean. Therefore, they have been associated with beauty and purity in Hinduism and Buddhism respectively, to name but a few cultures [10].



Figure 8. Dust on a lotus flower leaf [11].



Figure 9. Clean lotus flower leaf [12].

Lotus flower self-cleaning ability is due to its leaves microstructure which enhances superhydrophobicity and allows for suitable CAH [13]. Its hierarchical roughness features

papillas with diameters ranging from 5 μm to 9 μm and each one is covered by nanobranches which have a much smaller diameter $124.3 \pm 3.2 \text{ nm}$.

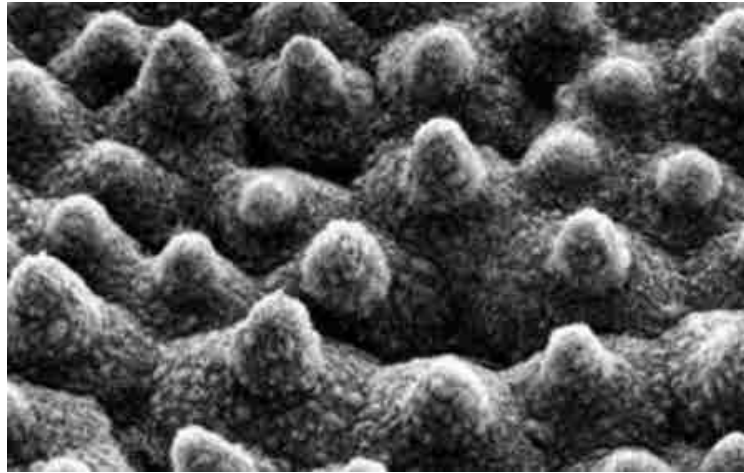


Figure 10. SEM image of a lotus leaf: surface hierarchical structure [13]

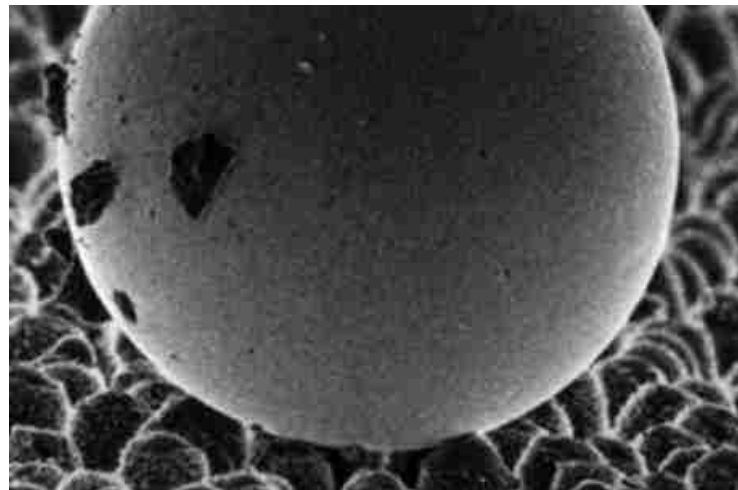


Figure 11. Water droplet collecting dirt particles [13].

3.1.5 Amphiphobic surfaces

In the passenger compartment many devices such as the touch screen of the satellite navigation system or the door handles, to name but a few, are subjected to touch. Therefore, they are stained with skin oil, fingerprint (oleic acid mainly) or sweat and have a bad aesthetic impact on the customer [14]. Thus we would like to have a superoleophobic surface because superhydrophobic ones in contact with oil spoil their superhydrophobicity [9]. Superoleophobic surfaces have a much lower surface energy than the superhydrophobic surfaces therefore they fulfill both tasks, repelling water and oil. The lower surface energy as well as the more complex geometry of the surface are the factors to address when looking for an amphiphobic surface. Low surface energy is achieved by means of special coatings such as organosiloxanes coatings [15]. Surface geometry is more complex than the superhydrophobic one because hierarchical roughness is not enough.

3.1.6 Superhydrophilic surfaces: photocatalysis

Surface coatings containing TiO₂ lead to self-cleaning through photocatalysis as anticipated in Figure 2. The working principle is different from that of the superhydrophobic surfaces because in this case the TiO₂ acts as a catalyst for organic compounds decomposition.

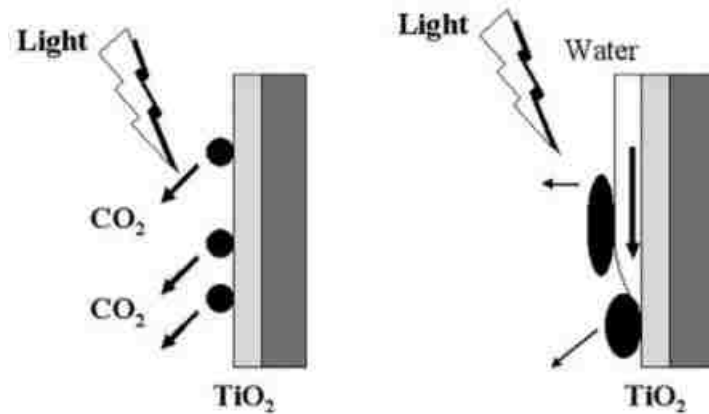


Figure 12. Decontamination process on the TiO₂ coated surface [16].

The photocatalysis process starts with the promotion of an electron from the valence band to the conduction band once it receives the energy $h\nu$ necessary to cover the energy gap E_g : where h is the Planck constant and ν is the frequency of the of the light waveform as can be seen in Figure 12. The conduction band electron can:

- Recombine with the hole left in the valence band and the input energy is dissipated as heat.
- Get trapped in “metastable surface states”.
- React with electron acceptors and the holes with electron donors.

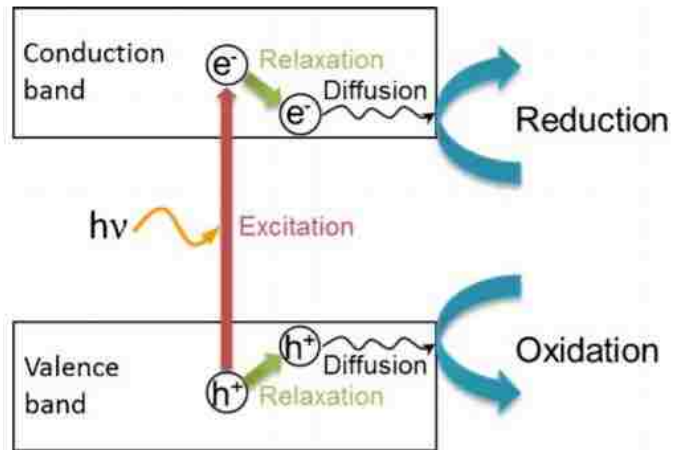


Figure 13. Charge carriers generation upon UV light absorption [17].

Both reduction and oxidation reactions must take place in order to avoid charge build up [18]. The holes can [17]:

- Directly oxidize organic compounds adsorbed on the surface.
- React with water to form hydroxyl radicals that together with the holes oxidize the organic compounds adsorbed on the surface.
- Weaken the bond between oxygen and titanium in TiO_2 and lead to the generation of OH groups leading to a hydrophilic surface [16].

As mentioned before the TiO_2 photocatalysts need UV light but their operating range can be extended to visible light if properly doped.

3.2 Particles adhesion on surfaces

As stated at the beginning the aim of the present work is to investigate what could be the materials and textures that would prevent particles from adhering to the surface. Therefore, an understanding of the types of interaction that occur is introduced in the following. There are five types of interactions that occur in particle adhesion:

- Molecular interaction
- Electrostatic interaction
- Liquid bridges
- Double layer repulsion
- Chemical bonds

3.2.1 Molecular interactions

Molecular interactions are based on the Van der Waals interactions. According to Van der Waals theory atoms in bodies are instantaneous dipoles and they induce dipoles in the neighboring atoms as well. The interactions are summed over all atoms of one body. The instant dipole and induced dipole phenomenon happens also between two bodies and originates the formation of the interactions.

The adhesion force between two bodies depends on their geometry and on the distance between them [19]. In the case of a sphere and a planar surface as in Figure 14 the adhesion force is given by eq.(1):

$$F_{ad} = \frac{A_{132}d_p}{12Z_0^2} \quad (1)$$

where:

- A_{132} is a constant of the material called Hamaker constant;
- d_p is the particle diameter;
- Z_0 is the distance between the sphere and the plane.

As can be seen the adhesion force increases with the particle diameter and with the inverse of the distance.

In the case of a cylindrical particle the adhesion force is expressed as force per unit length is to be considered as in eq.(2):

$$\frac{F_{ad}}{length} = \frac{A_{132}\sqrt{d_c}}{16Z_0^{5/2}} \quad (2)$$

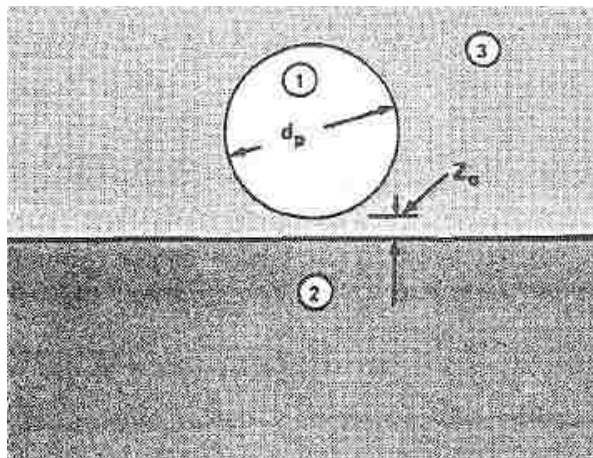


Figure 14. Van der Waals interaction between a sphere and a planar surface [19].

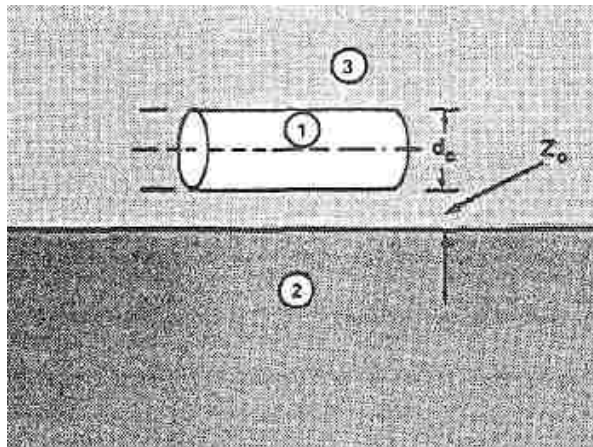


Figure 15. Van der Waals interaction between a cylinder and a planar surface [19].

In case of two planar surfaces the adhesion force is expressed as force per unit area as in eq. (3):

$$\frac{F_{ad}}{area} = \frac{A_{132}\sqrt{d_c}}{6\pi Z_0^3} \quad (3)$$

These three cases represent ideal situations, yet they are useful for an immediate understanding of the importance of the particle size and distance with respect to the surface.

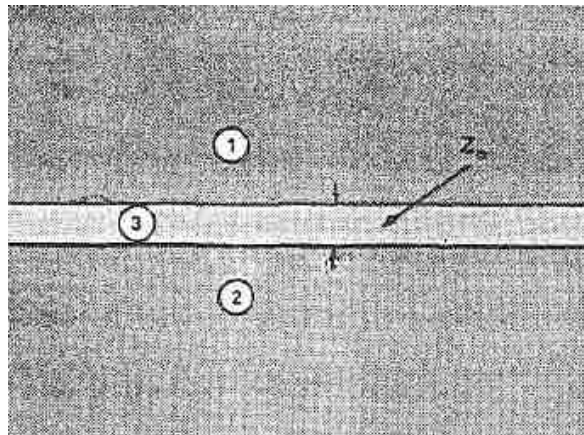


Figure 16. Van der Waals interaction between two planar surfaces [19].

3.2.1.1 Material hardness and surface roughness influence

Material hardness and surface roughness play an important role in particle adhesion. Material hardness influences the deformation of the contact zone between a particle and the surface. As the hardness increases the contact area decreases, thus the distance between the particle and the surface increases. This leads to a lower adhesion force. A softer material on the other hand allows a higher compliance between its surface and the particle, which leads to a lower distance and a higher adhesion force.

Surface roughness as well as material hardness influence the distance between the particle and the surface. Being that molecular interactions involve the atoms in the first nanometers of both bodies the entity of the roughness does influence the adhesion force. If surface asperities are much smaller than the particles dimensions, the adhesion force is low because the two bodies are far from each other, recalling that we are reasoning in terms of nanometers.

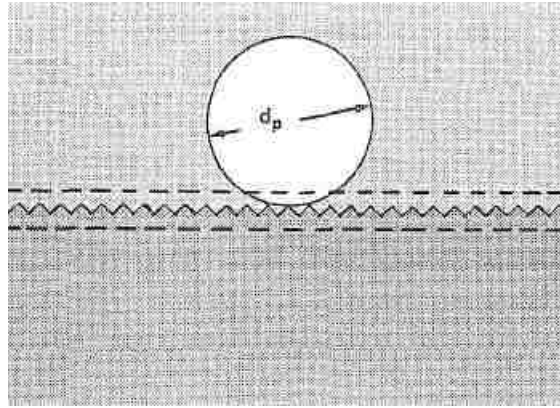


Figure 17. Surface roughness asperities smaller than the particle size [19].

On the other hand if the surface asperities are bigger or comparable with the particle size the two bodies may be closer to each other and a higher adhesion force may occur. A more detailed investigation of the roughness at a nano scale level can tell whether it increases or not because it is necessary to know what the distance is and it is not always easy to compute.

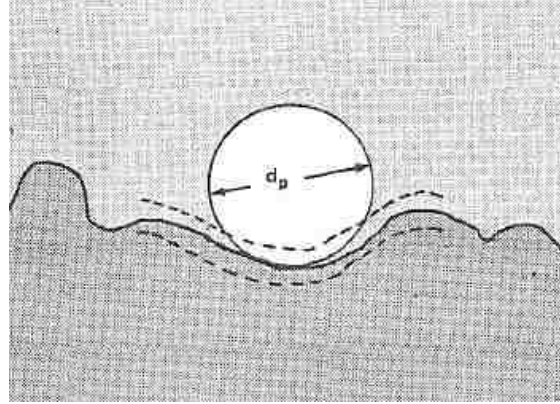


Figure 18. Surface roughness asperities smaller than the particle size [19].

Van der Waals interactions regard molecules in the first nanometers of the surfaces. They only interact with molecules from the bulk material beneath therefore, they have an unsatisfied bonding potential which results in an increased energy at the surface with respect to the bulk material. Surface energy can express the possibility for the surfaces to undergo Van der Waals interactions. Work of adhesion can thus be defined as the work necessary to separate the adhesive from the substratum in a given medium [20] and is expressed by eq. (4):

$$W_{132} = W_{12} + W_{33} - W_{13} - W_{23} = \gamma_{13} + \gamma_{23} - \gamma_{12} \quad (4)$$

where:

- W_{132} is the work of adhesion of media 1 and 2 in medium 3;
- $W_{i,j}$ is the work of adhesion of media i and j in void
- $\gamma_{i,j}$ is the surface interfacial tension between the surfaces and depends on the surface tension of each surface.

It can be observed that the lower the surface energy of the surface, the lower the work of adhesion, therefore a weaker adhesion will result [21].

3.2.2 Electrostatic interactions

Electrostatic interactions occur due to the attraction between charges of opposite polarity. There are two types of interactions that may arise:

- Contact potential difference generated interaction.
- Coulomb interaction due to electrically charged particles.

3.2.2.1 Contact potential difference generated interaction

The contact potential difference between two surfaces is the potential difference between them and depends on the difference between the work functions of the two materials. The work function of a material is expressed by eq.(5):

$$W = -e\Phi - E_F \quad (5)$$

where:

- W is the work function
- e is the electron charge
- Φ is the electrostatic potential in the vacuum in the vicinity of the material
- E_F is the Fermi level inside the material

The Fermi level inside a material is a well-defined constant for a material in thermodynamic equilibrium [22]. However, variations of E_F between samples of a same material may occur due to internal as well as external factors such as the purity of the material and its surface roughness [23].

The contact potential difference causes charge accumulation on the two surfaces and the resulting attraction force is expressed by eq.(6):

$$F_{el} = \pi\epsilon_0 \frac{d_p}{2} \cdot \frac{\Phi_C^2}{Z_0} \quad (6)$$

where:

- ϵ_0 is the dielectric constant of the medium between the surfaces;
- d_p is the particle diameter assuming a spherical particle;
- Φ_C is the contact potential;
- Z_0 the distance between the particle and the surface.

This interaction force may be comparable to Van der Waals force provided that the contact potential $\Phi_C = 0.5V$, the distance $Z_0 = 4 \text{ \AA}$, particle diameter $d_p = 1\mu\text{m}$ and Hamaker constant smaller than 1 eV; therefore it must not be neglected.

3.2.2.2 Coulomb interaction due to electrically charged particles

The interaction between an electrically charged particle and a metallic surface is assumed to be equal to that between the particle and its image inside the body as in Figure .

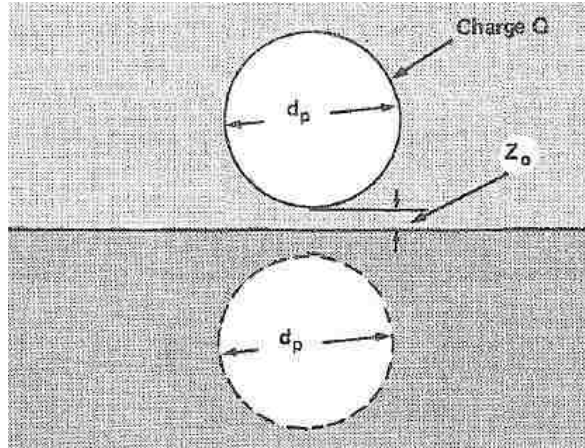


Figure 19. Electrical interaction between a particle and its image inside the body [19].

The interaction force according to Coulomb law can be expressed as in eq.(7):

$$F_{Ad} = \frac{Q^2}{6(d_p + Z_0)^2} \quad (1)$$

where Q is the electric charge of the particle.

Interactions due to electrically charged particles are stronger than those due to contact potential difference and as can be seen in eq. (1) they increase as the particle dimensions decrease. Electrostatic interactions due to both, electrically charged particles and contact potential difference, are significant when dealing with polymers because of their little charge leakage, that otherwise lowers the strength of the interactions, and Hamaker constant lower than 1 eV.

3.2.3 Liquid bridges: capillary condensation

For relative humidity values of 60-70 % water vapor can condensate in the gap between two bodies as shown in Figure 20. The meniscus formed in such a way attracts the bodies together due to surface tension [20].

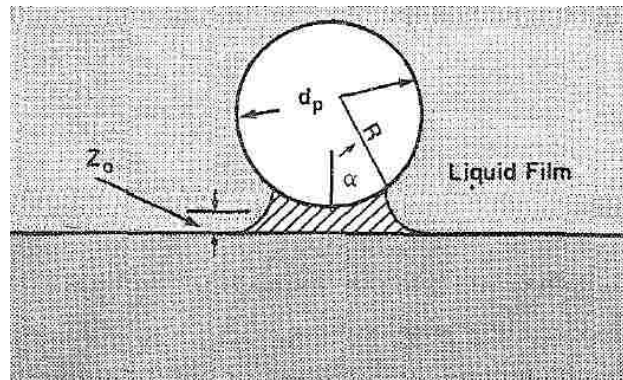


Figure 20. Capillary condensation [19].

3.2.4 Double layer repulsion

Double layer repulsion forces occur when the particles and the surface are immersed in an electrolyte solution. Any charge on the surfaces will attract ions of the opposite sign which on turn will be surrounded by another external layer of opposite sign ions in order to reach overall neutrality. Nevertheless, a potential gradient is established and it gives rise to an attraction or repulsion force according to the distance between the two interacting bodies [20].

3.2.5 Chemical bonds: acid-base interactions

Acid-base interactions occur due to the presence of acid-base sites on the surfaces of the interacting bodies. They are particularly relevant for polymers and occur due to the complementary structures of the acid-base sites and their opposite charge [24].

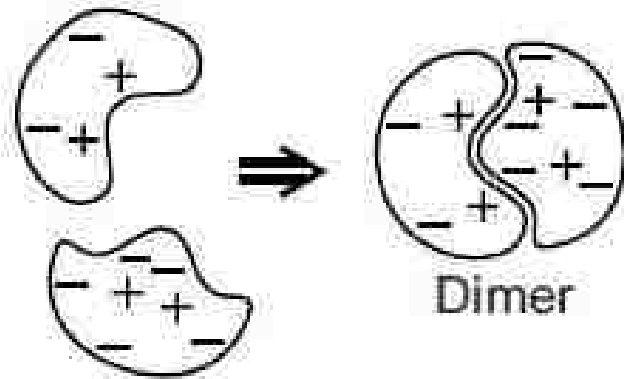


Figure 21. Acid-base interaction [24].

3.3 Polymers

Over the past decades global warming, pollution and fuel consumption have been hot issues for the automotive industry. Pollution reduction can be addressed by improving combustion processes, by reducing fuel consumption and by adopting post treatment systems. Global warming is due to the accumulation of greenhouse gasses such as CO₂ which is the product of the combustion of fossil fuels. Therefore, the only way to reduce its emission is by reducing fuel consumption. Fuel consumption reduction can be achieved by means of more efficient engines, smaller supercharged engines with a higher specific power (downsizing) and lower vehicle mass. In order to reduce the vehicle mass long chain polymers have been used as a substitute of metals. It has been estimated that 7% fuel reduction can be achieved by 10% vehicle mass reduction [25][26]. Other advantages obtained by the use of polymers are related to production investments, production rates, more sophisticated designs and enhanced safety [27][26][25]. Their main drawbacks are the low stiffness and impact strength, flammability and deterioration by thermal and environmental action. In order to obtain the required mechanical and thermal characteristics reinforcing agents and fillers are adopted.

Nowadays from 15% to 20% of the mass of a vehicle is due to polymer materials and the most common applications are: bumpers, grills, door structures, interior trims and instrument panel [28] and more as can be seen in Table 1 and Table2.

Table 1. Polymers adopted in automotive applications [26].

Part	Main Plastic Type	Weight in Average Car (kg)
Bumpers	PP, ABS, PC	10.0
Seats	PUR, PP, PVC, ABS, PA	13.0
Dashboard	PP, ABS, PA, PC, PE	15.0
Fuel Systems	PE, POM, PA, PP	7.0
Body (Including body panels)	PP, PPE, PBT	6.0
Under the Hood Components	PA, PP, PBT	9.0
Interior Trim	PP, ABS, PET, POM, PVC	20.0
Electrical Components	PP, PE, PBT, PA, PVC	7.0
Exterior Trim	ABS, PA, PBT, ASA, PP	4.0
Lighting	PP, PC, ABS, PMMA, UP	5.0
Upholstery	PVC, PUR, PP, PE	8.0
Other Reservoirs	PP, PE, PA	1.0
	Total	105.0

Table 2. Applications of polymers in the automotive field [26].

Polymer Name	Properties	Application Examples
Polypropylene	Low-cost, good solidity, chemical resistance	Bumpers, wheel housings, air filter housings, guide channels, containers, side panels, battery case, door trim, crash panel
Polyurethane	Damping, good elasticity, low heat conductivity	Seat upholstery, dashboard and roof padding, exterior elements
Acrylonitrile Butadiene Styrene Copolymer	Electroplatable, dimensionally stable, solid	Interior paneling, wheel panels, radiator grills, dashboard
Polyamide	Temperature-stable, low gas permeability, permanently solid, rigid, ageing-resistant	Motor covering, suction elbows, wheel panels, plugs, mirror housing, door handles, connector housing
Polyvinylchloride	Weather-resistant, low-cost, non-inflammable, good haptics	Underbody protection, protective bordering, cable insulation, interior paneling
Polyethylene	Low-cost, ageing-resistant, chemical resistance, good solidity	Fuel tanks, windshield fluid containers
Polyoxymethylene	Chemical resistance, abrasion-resistant, impact-resistant, low tendency to creeping, thermally stable	Clips, connectors, bearing components
Polymethylmethacrylate	Transparent, scratch-resistant, UV-resistant, stress-cracking resistant	Headlight lenses for blinker and rear lamps
Polycarbonate	Impact-resistant, transparent, UV-resistant	Headlight lenses, tail light cover, bumper coverings, exterior auto body parts
Polyethyleneterephthalate	Tensile strength, rigid, good barrier effect	Textiles, coverings, seat belts, airbags
Polybutyleneterephthalate	Rigid, heat-resistant, good electrical insulating, behavior, dimensional accuracy	Electronic housings, bumper coverings, exterior auto body parts, plugs, connector housing
Polyetheretherketone	Heat-resistant, friction-wear properties, chemical resistant	Oil pump, bearing, washer, transmission parts, ball joint, brake parts



Figure 22. Dodge Charger polypropylene bumper [29].

The use of polymers in automotive applications is also restricted by environmental and safety regulations. Environmental regulations are related to recycling and to life cycle considerations: USA as well as E.U. and Japan released stringent guidelines for what concerns the percentage of the vehicle that should be recycled [25]. Safety regulations are related to crashworthiness, energy absorption with a gradual decay in the load profile during absorption, and penetration resistance, the total absorption without penetration of fragments in the passenger compartment. Last but not least customers' perception of the adopted plastics is a strong constraint and stimulus for continuous improvement because the aesthetic appeal is an important factor in the decision making process.

3.3.1 Polyamides

There exists a wide variety of thermoplastic polymers classified as polyamides. Their common feature is the amide group (- CONH-) which occurs repeatedly in the polymer chain. They are linear polymers with good propensity towards crystallization. The amide group increases the resistance to swelling and the interchain attraction, therefore the stiffness and the heat deformation resistance. On the other hand it increases water absorption by the polymer and negatively influences electrical insulation.

The variables affecting the characteristics of polyamides are:

- The distance between two consecutive (-CONH-)

A higher concentration of the amide groups causes an increase of the tensile strength, rigidity, hardness and creep resistance of the polymer. It is beneficial also for the thermal characteristics with an increase in the melt temperature T_m and the heat deflection temperature. The drawback is an increase of water absorption.

- Number of CH_3 groups in the intermediate

It has been observed that polymers with an odd number of CH_3 groups have lower mechanical and thermal properties with respect to those with an even number of methyl groups. This is due to the fact that during crystallization the oxygen of one molecule is closer to the amide group of another molecule when they have an even number of CH_3 groups.

- N- Substitution

The replacement of the hydrogen in the amide group with a methyl group or other functional groups may decrease the intermolecular interactions.

- Percentage crystallinity

It has been observed that an increase in the degree of crystallinity increases the mechanical properties and decreases water absorption.

3.3.1.1 Glass filled polyamides

Glass filled polyamides have been designed in order to reduce the performance gap between thermoplastics and metals. They can be divided into glass-fibre-filled and glass-bead-filled polyamides. Both grades contain up to 40% of glass fibers and show significant improvements in mechanical and thermal properties as can be seen in Table 3.

Table 3. Comparison between of a glass-filled and unfilled polyamide, nylon 66.

<i>Property</i>	<i>Units</i>	<i>ASTM test</i>	<i>Glass-filled</i>	<i>Unfilled</i>
Specific gravity	–	D.792	1.38	1.14
Tensile strength	10^3 lbf/in^2 (MPa)	D.638	23 159	11.5 79
Elongation at break	%	D.638	3–5	80–100
Flexural modulus	10^5 lbf/in^2 (MPa)	D.790	11 8000	4.3 3000
24 h water absorption at saturation	%	D.570	5.6	8.9
Coefficient of linear expansion	in/in °F (cm/cm °C)	D.696	1.65×10^{-5} 2.8×10^{-5}	5.6×10^{-5} 9.9×10^{-5}
Deflection temperature under load				
66 psi	°C	D.648	254	200
264 psi	°C	D.648	245	75

Glass-bead-filled polymers compared to glass-fiber-filled ones are easier to process due to their lower melt viscosity, warpage and more predictable shrinkage. Furthermore, they have a better degree of isotropy for what regards their mechanical properties. Both grades usually have better self-extinguishing characteristics than the unfilled polyamide formulation.

3.3.2 Polypropylene

Polypropylene is a polymer molecule composed by propylene monomer units. It is available in different yields from the cracking of petroleum as a co-product with ethylene. The main advantages of polypropylene are:

- excellent chemical resistance
- excellent environmental stress crack resistance
- non-hygroscopicity
- good insulation
- good impact/stiffness balance
- low density

Due to its properties polypropylene has a broad range of applications such as packaging, textiles, film, automotive, electrical and medical. Furthermore, it is suitable for almost all the conversion processes: blow molding, extrusion, injection molding, compression molding and all types of fiber processes.

There are five factors that influence the properties of polypropylene: molecular weight, molecular weight distribution (for homopolymers), crystallinity, additive package and comonomer content. An increase in molecular weight causes a higher melt viscosity and melt flow rate, and a higher toughness. Molecular weight distribution can be narrow or broad. A narrow molecular weight distribution causes a lower warpage during processing, a higher impact strength and a higher elongation at break. On the other hand a polymer formulation with a broad molecular weight distribution is characterized by a better injection molding processing and leads to a stiffer end product.

Polypropylene is a semi-crystalline polymer and its amount of crystallinity is influenced by the polymer structure, by the fillers or additives in the formulation as well as by the processing conditions. The advantages of an increased crystallinity are:

- better heat, scratch and stain resistance;
- higher stiffness;

- lower production cycle time.

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- molecular weight,
- molecular weight distribution (for homopolymers),
- crystallinity,
- additive package,
- comonomer content.

An increase in molecular weight causes a higher melt viscosity and melt flow rate, and a higher toughness. Molecular weight distribution can be narrow or broad. When it is narrow the part will undergo a lower warpage during processing and it will have a higher impact strength and a higher elongation at break. On the other hand a polymer formulation with a broad molecular weight distribution is characterized by a better injection molding processing and it will lead to a stiffer end product.

Polypropylene is a semi-crystalline polymer and its amount of crystallinity is influenced by the polymer structure, by the fillers or additives in the formulation as well as by the processing conditions. The advantages of an increased crystallinity are:

- better heat, scratch and stain resistance,
- higher stiffness,
- lower production cycle time.

Numerous chemicals can be added to the resin. They can be subdivided into stabilizers, which help the polymer to maintain its properties, and additives which enhance the properties of the resin. The most used chemicals with polypropylene are the nucleating agents used to increase the stiffness and reduce cycle time, the clarifiers which increase the transparency of the polymer, the slip agents which reduce the friction between the polymer and the machines allowing a lower cycle time, and antioxidants that help the polymers to withstand the high heat needed to pelletize and process the resin.

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Polypropylene structures can be classified according to the increasing ethylene content as homopolymer, random copolymer and impact copolymer. The homopolymer does not have ethylene in its chain. It is characterized by a higher crystallinity and stiffness than the other structures. On the other hand it features the lowest impact strength. The random copolymer contains up to 6% of ethylene which disrupts structural regularity and reduces crystallinity. This improves impact strength and clarity, yet it reduces the stiffness of the polymer. The impact copolymer contains up to 25% of ethylene which leads to a further room and low temperature impact resistance increase with respect to the polypropylene random co-polymer.

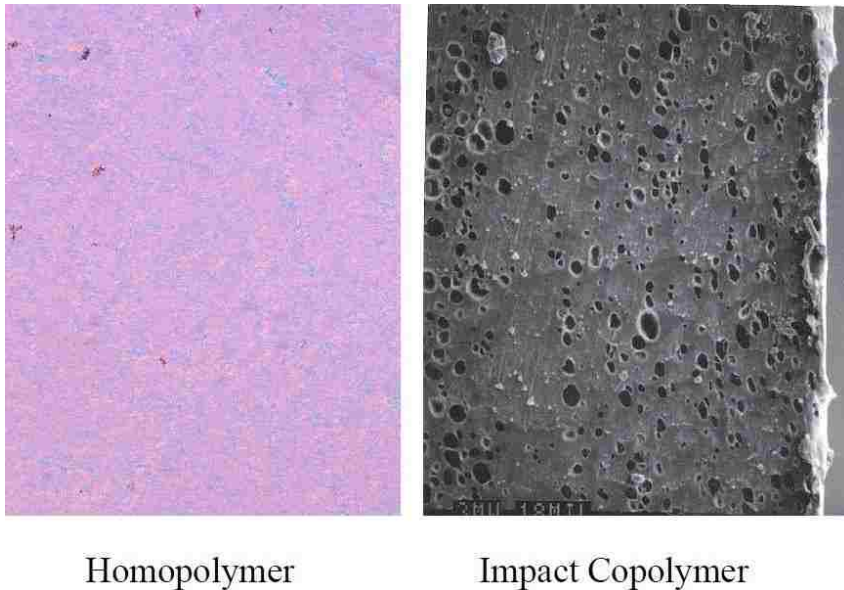


Figure 23. Polypropylene morphologies comparison [54].

3.3.3 Thermoplastic polyolefins

Thermoplastic polyolefins are produced by very similar process to polypropylene but with an additional step in which more ethylene is added, to a total of more than 20% in the formulation. The further addition of ethylene vastly improves the impact properties.

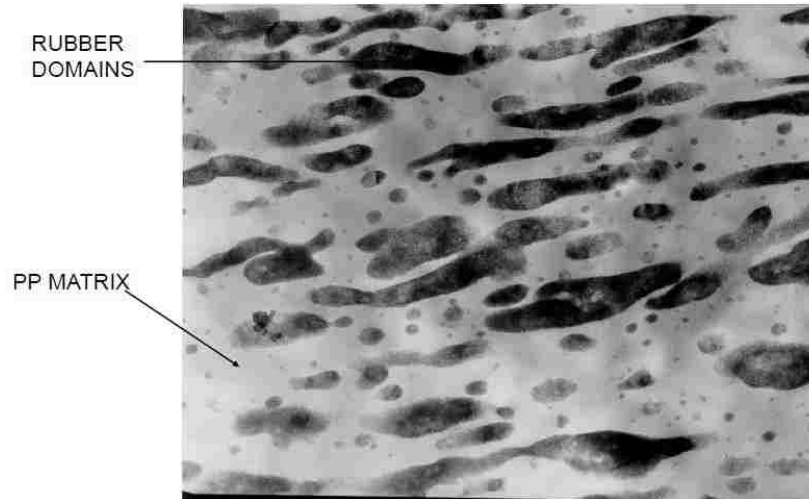


Figure 24. TPO morphology [54].

The main advantages of thermoplastic polyolefins are:

- very good impact properties,
- easy recyclability,
- lowest total system cost when compared to other thermoplastics or thermosets.

As seen with the polypropylene, also the thermoplastic polyolefins can be modified by adding to it fillers, pigments, stabilizers or other additives as can be seen in Figure 25. It is possible to identify three key formulation components for the TPO: the polypropylene, the elastomer and the fillers. Polypropylene provides dimensional stability and chemical and heat resistance. On the other hand it reduces impact strength at low temperature. The elastomer is used in order to improve the low temperature impact performances, yet is also enhances the flexibility of the polymer and improves its paintability.

<u>Olefin Resin</u>	+	<u>Rubber</u>	+	<u>Filler</u>	+	<u>Additives</u>
- PP homopolymer		- EPDM		- Talc		- Anti-oxidants
- PP copolymer		- EPR		- Calcium carbonate		- UV Stabilizers
		- Specialty Elastomers		- Glass fiber		- Processing aids
						- Pigments

Figure 25. Generic composition of TPO [54].

It is important to mention that the elastomer reduces the mar and heat resistance and it can also affect the color of the natural compound. Fillers are used to control the flexural modulus of the TPOs. They also provide a better shrinkage control, a better dimensional stability and an enhanced heat resistance under load. Since their price is lower than the price of the resin the fillers allow a cost reduction as well. On the other hand the addition of fillers causes an increase of the specific gravity of the polymer and reduces its low temperature impact strength.

<u>Physical Property</u> <u>Increase in....</u>	<u>Rubber</u>	<u>Talc</u>	<u>PP</u>
Impact strength	↑	↓	↓
Stiffness	↓	↑	↑
Mold shrinkage	↓	↓	↑ ↓
Heat Deflection	↓	↑	↑
Density	↔	↑	↔

Figure 26. Influence of the fillers on the physical properties of the TPO [54].

4. Methodology

In this chapter, a description of the polymers adopted is provided and the test methodologies are explained.

4.1 Materials

The materials provided for testing are different compositions of three main thermoplastic polymers: thermoplastic polyolefins, polypropylene impact copolymers and polyamides. They are utilized in different areas of the passenger compartment according to the requirements of those specific applications. The polypropylene is used in interior hard trim plastic applications such as seat side shields, door sills and quarter trim panels, which do not require high impact or stiffness. The thermoplastic polyolefin is used in the instrument panel, console panel and door trim where high impact strength and stiffness is required: this material has 20% talc to counter the lower stiffness do to impact. The polyamide is used for the doors handles where very high stiffness and strength is required.

Each material comes in two colors, light and dark, and has different additives and fillers. The baseline formulation of the polypropylene is indicated as PP, that of thermoplastic polyolefin as TPO and that of the polyamide as PA6.

Table 4. Materials tested.

	Material		
	TPO	PP	PA
Light	Base, 1,2,4,5	Base, 1,2,4,5	6, 1, 2
Dark	Base, 1,2,3,4,5	Base, 1,2,3,4,5	6, 1, 2

The material was provided in the form of a glovebox instead of individual flat coupons because the molding process influences the final results. Therefore, even if made of the same material, a glovebox will have different characteristics than a coupon even if the latter is much easier to be tested. The gloveboxes were tested as they came from the supplier. Their initial cleanliness was visually assessed and no preliminary cleaning was performed in order to replicate more accurately the scenario in the passenger compartment. The operators carefully handled them in order not to touch the textures on the surface. Each glovebox had eleven different textures as can be seen in Figure 27. A magnification of each texture is provided in Figure 28 Figure 38.



Figure 27. Dark glovebox with eleven textures.

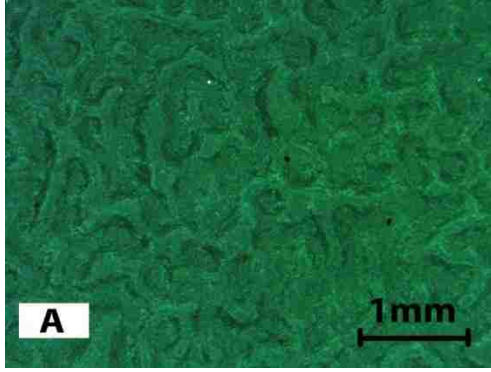


Figure 28. Texture A.

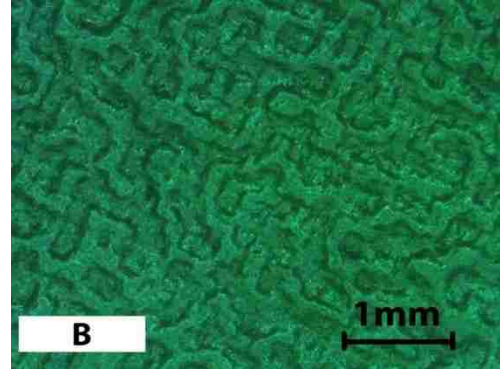


Figure 29. Texture B.

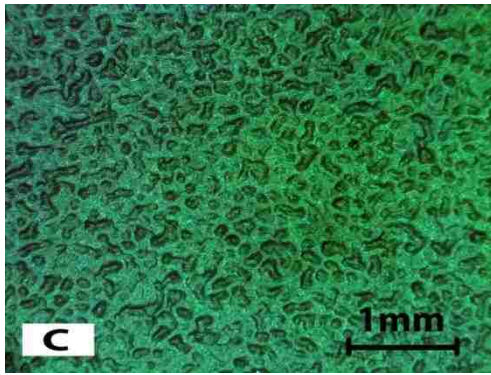


Figure 30. Texture C.

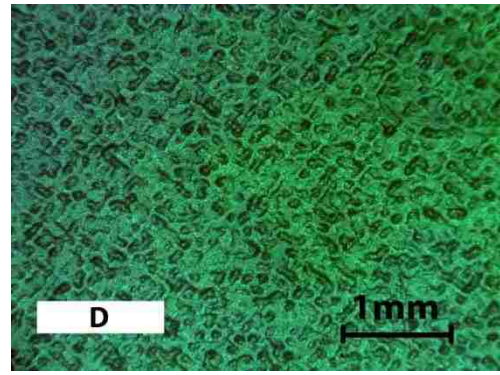


Figure 31. Texture D.

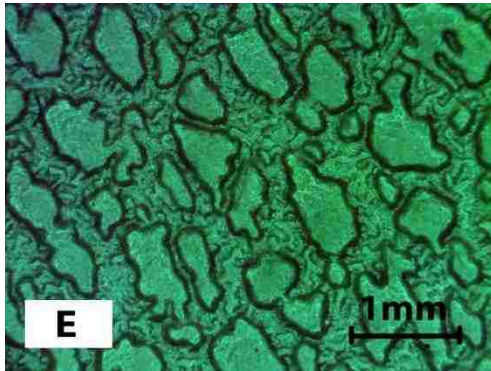


Figure 32. Texture E.

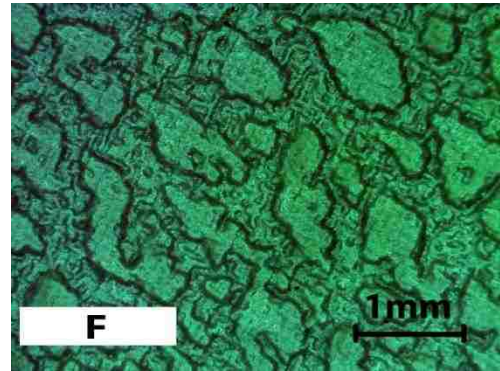


Figure 33. Texture F.

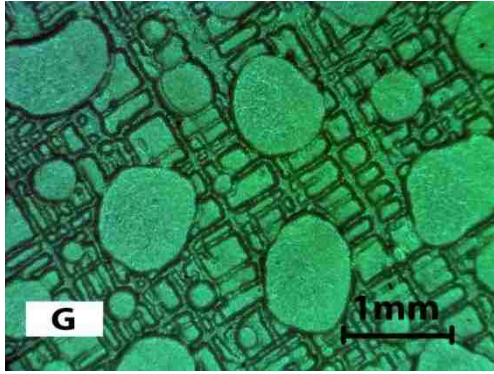


Figure 34. Texture *G*.

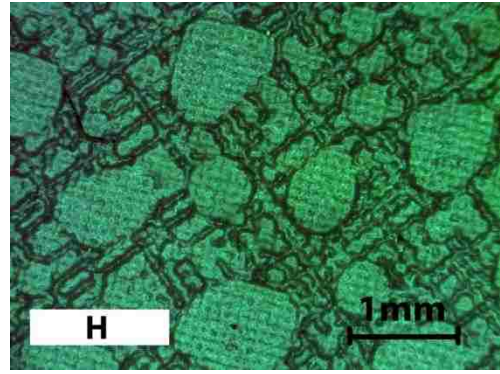


Figure 35. Texture *H*.

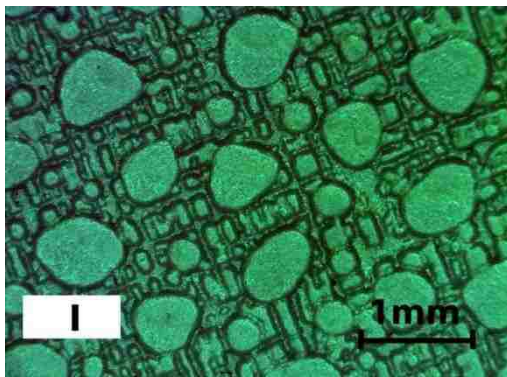


Figure 36. Texture *I*.

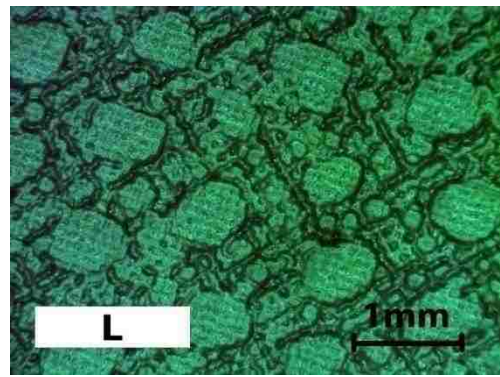


Figure 37. Texture *L*.

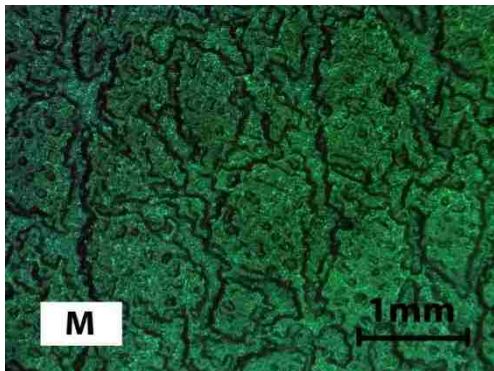


Figure 38. Texture *M*.

4.2 Flexural modulus

The supplier of the base resins (TPO, PP and PA) provided the material sheet of each resin. The material properties of each one slightly differ from the others in the way they were measured. The only property measured in the same condition is the flexural modulus, which has been evaluated according to the ISO 178 at 23° Celsius.

The flexural modulus is an intensive property of the materials which defines the ability of resisting deformation under load. It is measured as the ratio between stress and strain in the deformation of a beam placed on two supports on which a vertical load is applied at midspan [45] as in Figure 39.

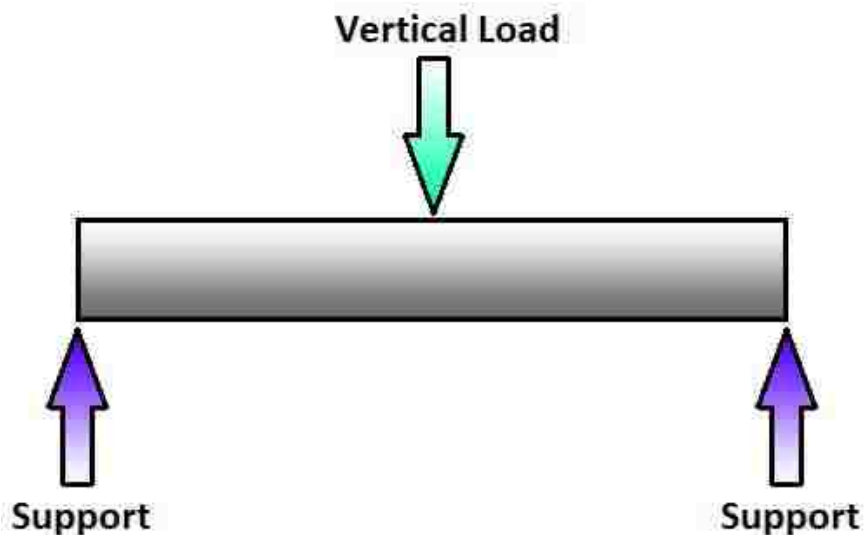


Figure 39. Flexural modulus measurement layout.

Table 5. Flexural modulus of the base resins.

	PP	TPO	PA
	[MPa]	[MPa]	[MPa]
Flexural Modulus	1100	1850	8600

4.3 Soiling tests

Soiling of the plastic components in the passenger compartment may be due to many different sources. Three main soiling scenarios have been identified for the purpose of this study:

- Dust deposition on the plastics in the passenger compartment

Dust deposition is of concern in dusty environments such as the countryside due to the unpaved roads and the fields. The dust may get into the passenger compartment because it can be carried in by the wind when the doors or windows are opened, or it can stick to our shoes and then be deposited in the lower part of the passenger compartment: a subsequent air motion, as the one induced by the climate system vent, can then move the dust all over the cabin.

The test methodology adopted in order to investigate dust deposition is called Dusting test.

- Dust brought in contact with the plastics by the cloths

The dust can adhere to the clothes of the driver and of the passengers. It is then brought in contact with the plastics when the clothes are rubbed against them. A typical scenario can be represented by soiled jeans rubbing against the knee bolster. The test methodology selected in order to examine the rubbing effect of a soiled cloth against a polymeric material is called Martindale test.

- Oily skin marks on the plastics

The skin naturally produces a waxy or oily matter, called sebum, in order to moisturize itself. Every interaction between the skin and the plastics in the passenger compartment involve soiling of the polymeric materials by the sebum and other substances and particles on the skin. A typical scenario is represented by the fingerprints on the dashboard and on the handles. The test methodology developed in order to study the oil and particles interaction with the polymers is called Fingerprint tests.

The test methodologies adopted in this study are described in the following subchapters..

In order to have a reproducible methodology the test was limited to a standard test dust and cloth impregnated with carbon black. The adopted test dust is the ISO 12103-1, A4 Coarse test dust. It is commonly used for fuel filter testing, air filter testing and abrasion testing [30]. Its composition is outlined in Table 6 and Table 7.

Table 6. ISO 12103-1, A4 components percentage [31].

CAS No	Components	Quantity
14808-60-7	silica (fine dust)	69-77 %
1344-28-1	aluminium oxide	8-14 %
1305-78-8	calcium oxide (mineral)	2.5-5.5 %
12136-45-7	potassium oxide (mineral)	2-5 %
1313-59-3	sodium oxide (mineral)	1-4 %
1309-37-1	Iron(III) oxide (hematite)	4-7 %
1309-48-4	magnesium oxide	1-2 %
13463-67-7	titanium dioxide	0-1 %

Table 7. ISO 12103-1 A4 coarse, particles sizes [31].

ISO 12103-1 ARIZONA TEST DUST CONTAMINANTS A4 COARSE GRADES	
Iso Test Dust Particle Size Distributions by Volume %	
<i>Size Micrometer</i>	<i>ISO 12103-1, A4 Coarse Test Dust % Less Than</i>
0.97	0.74 – 0.83
1.38	1.8 – 2.1
2.75	5.5 – 6.3
5.50	11.5 – 12.5
11.00	21.0 – 23.0
22.00	36.0 – 38.5
44.00	58.0 – 60.0
88.00	85.0 – 86.5
124.50	93.0 – 94.0
176.00	97.2 – 98.2
248.90	99.0 – 100.0
352.00	100.0

The test cloth adopted for the test is an STC EMPA 106 soiling cloth. It is a cotton cloth soiled with IEC carbon black/mineral oil with a density of 200 g/m² [32].



Figure 40. STC EMPA 106 soiling cloth.

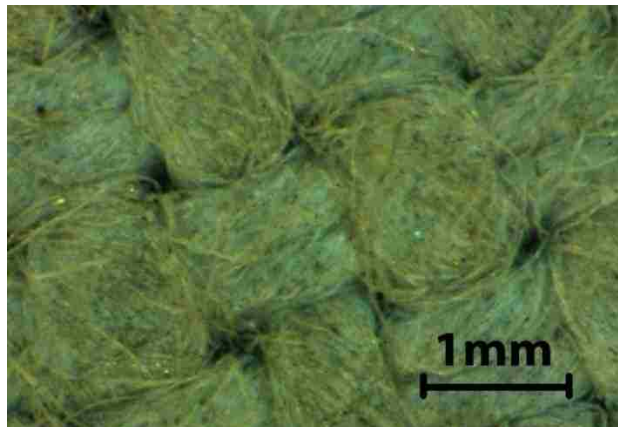


Figure 41. Soiling cloth magnification.

4.3.1 Martindale Test

Martindale tester is usually adopted for abrasion tests on cloths and soft trims [33][34]. In order to adapt it for suitable testing on polymers, the lower pads (already removed in Figure 43) have been removed and the samples hold into position by means of a bi-adhesive tape. According to an internal standard, 12 kpsi loads, 100 cycles and linear motion of the holders has been adopted as working parameters. The specimens were cut from the gloveboxes by means of a cutter. Soiling cloth and a foam material were cut in a round shape. The Martindale test is the test where the highest load is applied.



Figure 42. Cutter for specimens preparation.



Figure 43. Martindale Abrasion Tester.

4.3.2 Fingerprint Test

The fingerprint test was performed by an external supplier according to an internal standard for grease and dust collection on plastic surfaces. A rubber stamp with a metallic body and rubber soaked in mineral oil at one end is adopted for this test. A human operator pushes the stamp first against the ISO 12103-1, A4 Coarse test dust and then against one texture on the glovebox. The applied load is smaller than in the Martindale test. This operation is performed multiple time for each texture as can be observed in Figure 45. Each glovebox was then shaken prior to color measurements in order to get rid of the extra dust. For each texture the color difference was measured for the soiled area whose dust distribution was more homogeneous.



Figure 44. Fingerprint test: rubber stamp.



Figure 45. Fingerprint test: glovebox.

4.3.3 Dusting test

Dusting test was performed by an external supplier. The gloveboxes were taped on the middle in such a way to have half of each texture covered. Then ISO 12103-1, A4 Coarse test dust was sprinkled on the glovebox and let rest for a while. After that the glovebox was shaken to get rid of the extra dust. As can be inferred, no load was applied during soiling.



Figure 46. Dust sprinkled on a glovebox.



Figure 47. Glovebox after dusting test.

4.4 Spectrophotometry

The soiling of the specimens was measured as the difference in color between the clean and the soiled areas. Each color can be identified based on three elements: hue, chroma and lightness. The hue is the perceived color of an object (i.e. yellow, red, green, etc). The chroma describes the dullness or vividness of a color while the lightness the color intensity: the colors can be classified as dark or light according to their values of lightness.

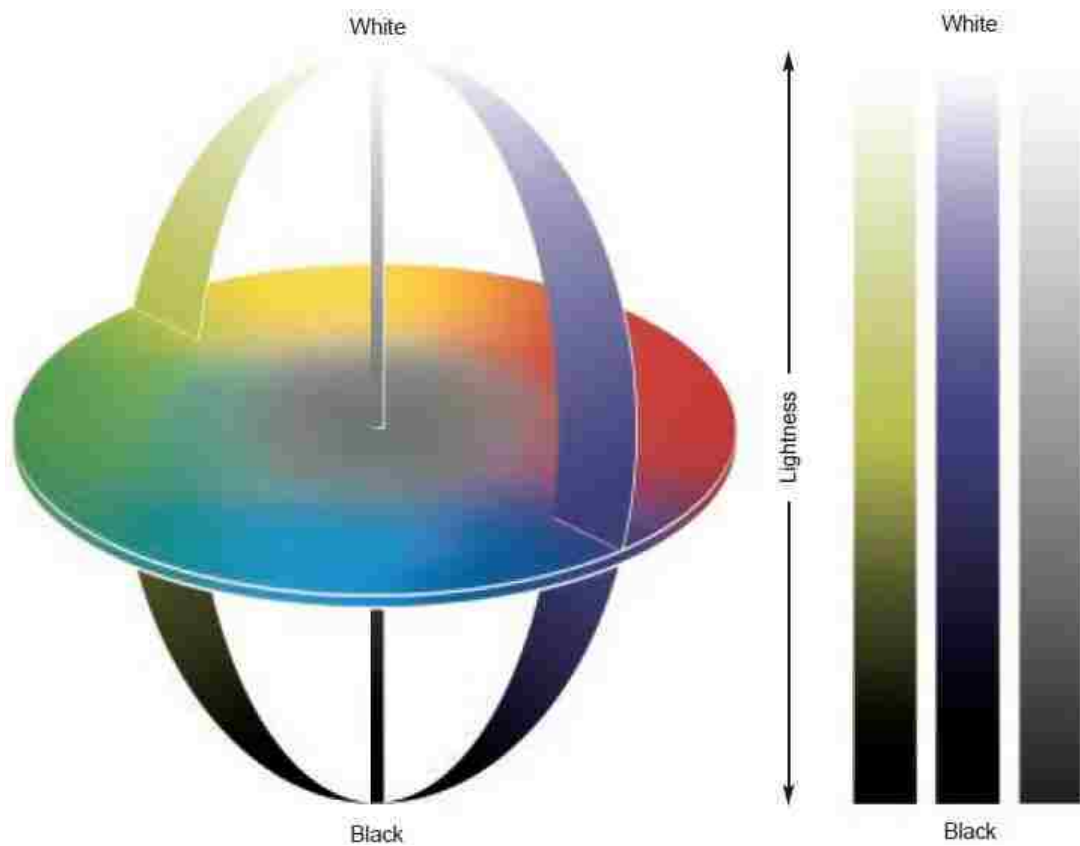


Figure 48. Three dimensional color system.

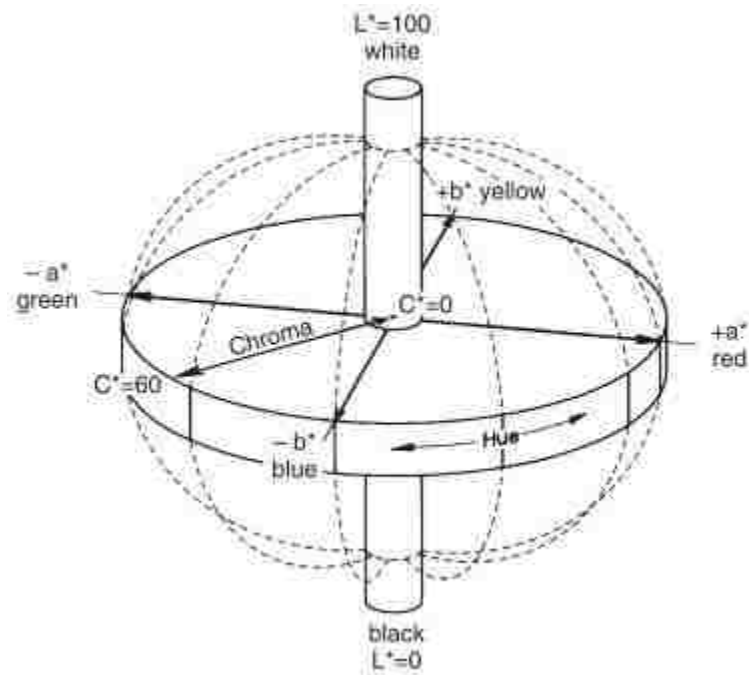


Figure 49. CIELAB color diagram with lightness axis [35].

From a physical point of view, the color of an object is the color of the light leaving its surface. It depends on the spectrum of the source of light, on the reflectance characteristics of the surface and on both the angles of viewing and illumination. Furthermore, the color perception changes from person to person because of the age, eye fatigue and other physiological factors. Thus, the need for a standardization in this field arose. The Commission Internationale de l'Eclairage (CIE) is the institution responsible for international recommendations for colorimetry and photometry. It has standardized the color order systems by specifying the observer, the light source and the methodology adopted in order to obtain the values for describing color. The CIE Color Systems introduced three coordinates to locate a color in a color space and three color spaces: CIE XYZ, CIELAB and CIELCH. A color in the CIE XYZ color space is represented by the three coordinates X, Y and Z whose computation is described in the following.

Color measurement instruments collect the light wavelengths reflected from an object and record them as points across the visible spectrum. Each point, also called spectral datum, is characterized by an abscissa value which is the wavelength and an ordinate value that corresponds to the percent reflectance. A low percent reflectance corresponds to a low contribution of a given wavelength in determining the color of an object and viceversa. The graphical representation of the spectral data is called spectral curve. In order to map the color onto a space it is necessary to multiply its spectral data by the CIE standard illuminant that corresponds to the light source under which the samples are observed. It is of importance to remark that each light source has its specific power distribution. This affects color perception since the power of the reflected light wavelengths depends on the power of the incident ones. The results of this calculation are multiplied by the CIE standard observer which represents how an average person perceives colors. The final result is then converted into the tristimulus values X, Y and Z. The CIELAB and CIELCH color spaces are preferred to the CIE XYZ because while Y relates to lightness, X and Z do not relate to the hue and chroma.

The CIELAB color spaces uses the cartesian coordinates L^* , a^* and b^* . In particular L^* defines lightness, a^* denotes the red/green value and b^* the yellow/blue. Therefore, the hue and the chroma can be identified by the coordinates a^* and b^* as in Figure 49. The CIELCH color space uses the polar coordinates L^* , C^* and h° . They can be derived from the CIELAB scale coordinates. In particular L^* specifies the lightness, C^* denotes the chroma and h° defines the hue angle. The advantage of the CIELCH over CIELAB scale is that the L^* , C^* and h° relate very easily to the color systems based on physical samples. In this study the colors have been expressed in CIELAB scale. The color difference between two objects according to the CIELAB scale can be stated as a single value called total color difference value and indicated as ΔE^* . It can be computed according to eq.(8):

$$\Delta E^* = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \quad (8)$$

where ΔL^* , Δa^* and Δb^* are the difference between the color space coordinates of each object [35].

The color measurement was performed using a portable spectrophotometer which determines the CIELAB color space coordinates. The adopted device was spherically based because as found in literature it is suitable for color measurements on a rough, irregular or textured surface [35]. It also allowed for the exclusion of the specular component during measurements. Three measurements on each area (soiled and clean) at different orientations were performed. The differences of the color space coordinate (ΔL^* , Δa^* and Δb^*) were evaluated and for each set of coordinates the total color difference value was computed. Then the average of the three ΔE^* values was taken as representative of the total color difference value between the soiled and clean areas of each specimen.

The error on the average ΔE^* value has been considered as the standard deviation of the values used to compute the average [36]. However, the values of the standard deviation are of the same order of magnitude of the error of the spectrophotometer. Thus the error on the data in Chapter 5 is equal to 0.01, the intrinsic error of the spectrophotometer.

4.5 Surface energy evaluation

Surface energy has been evaluated from the measurements of the contact angle (WCA) between a droplet of distilled water and the surface of the specimens. The available means were not adequate for the task, therefore surface energy was not measured. Nevertheless, the wettability of a surface which can be assessed by the value of the WCA is strictly related to the surface energy. In particular a high value of the WCA occurs for low surface energy values and viceversa.

The adopted methodology requires a flat surface therefore, a flat stripe was cut from each specimen as shown in Figure 50. Then they have been washed in a solution which contained 10% in volume DAWN Original dishwashing liquid and water as indicated by an internal standard for the cleaning of polymers of a major OEM. After cleaning, they have been rinsed using tap water and then distilled water in order to eliminate any impurity from the tap water. Then the specimens were placed on a table to dry. The use of a hairdryer is not recommended because despite speeding up the drying process, its warm air may cause some surface modification, as the specimens are thermoplastic polymers.

The distilled water droplets have been poured on the specimens by mean of a syringe actuated by a syringe pump controller which allowed a precise calibration of the volume of each droplet and injection time. The volume of each droplet has been chosen to be 10 μL and the injection time 10 s, which are common values in literature [37]. A total of three droplets per specimen were deposited and a picture for each one taken by means of a microscope as in Figure 51. Each picture was then imported in AutoCAD where the tangent to the droplet in the contact point was drawn and its slope measured.



Figure 50. Flat stripes cut from each specimen.



Figure 51. Optical microscope and WCA measurement activity layout.

4.6 Surface hardness measurement

The surface hardness of each specimen was measured by means of a microhardness testing machine with a Vickers indenter [38][39]. The load was set to 10 gf because it has been observed that for higher values of the load, the diagonals of the indented area were as big as the indentation image or larger. For instance with 25 gf, the immediately higher load available for the adopted testing machine, the diagonals of the indented area were slightly smaller than the indentation image. The dwell time was set to 10s [39]. The hardness was calculated according to the ASTM standard E384 – 11 [40] starting from the lengths of the two diagonals of the indented area indicated as d_1 and d_2 in Figure 52. The diagonals were manually measured by means of a ruler embedded in the microindenter. Vickers hardness value was calculated using eq(2):

$$HV = 1854.4 \times P/d^2 \quad (2)$$

where HV is the hardness value, P is the force expressed in gf and d the average between the two diagonals of the indentation area.

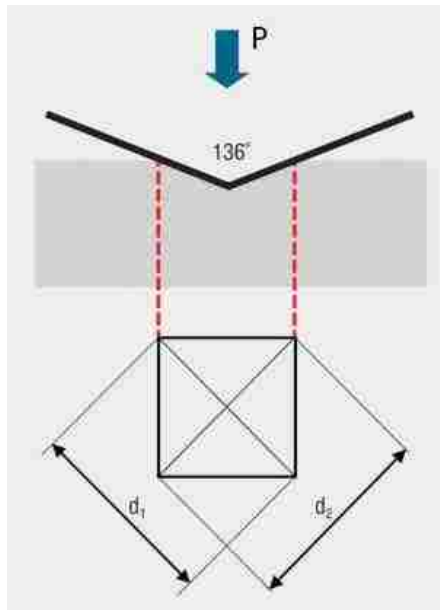


Figure 52. Vickers hardness indentation diagram [41].

5. Results and discussion

In this chapter the results of the experimental work are shown and discussed. In the first part, for each test methodology a comparison between the results of the same polymer category in dark and light formulations have been performed. Then the discrepancies of the three tests have been compared. Subsequently an analysis over all the polymers has been performed in order to understand which is the material and texture that show the smallest value of color difference. At the end, also hardness and surface energy evaluations are reported.

The majority of the tables reported in this thesis have colored cells. The colors range from green, for the specimens with the lowest color difference (ΔE^*), to red for those with the highest color difference (ΔE^*). From now on, the specimens with the lowest value of ΔE^* are referred to as the best performing ones, while those with the highest value of ΔE^* are referred to as the worst performing ones. The tolerance ranges for each shade of color are not constant over all the tables. Thus, the colors do not constitute a criterion for the selection of the specimens, but rather a visual means for a quicker interpretation of the results.

5.1 Martindale test – material effect

5.1.1 Martindale test - Dark Polypropylene

As we can see in Table 8 for Dark PP formulations, on average PP3, PP2 and PP behave considerably better, from the point of view of soiling prevention, than the base formulation (PP) while PP5 and PP1 much worse. Furthermore, the standard deviation of the PP3 formulation is lower than those of the PP5 and PP1. It is important to notice that the standard deviation of the baseline material (PP) is higher than those of the other materials, which means that the latter are more robust against texture variation. It can also be seen that the textures *D*, *B*, *A* and *E* have overall good performances on PP formulations.

Table 8. Martindale test - Dark polypropylene ΔE^* values.

Martindale test - Dark polypropylene - ΔE^* values								
Material Texture	PP5	PP4	PP3	PP2	PP1	PP	Average	StDev
D	0.48	0.53	0.21	0.44	0.59	0.17	0.40	0.16
C	0.47	0.40	0.17	0.63	0.66	0.27	0.43	0.18
B	0.55	0.45	0.31	0.20	0.61	0.25	0.40	0.15
A	0.52	0.44	0.22	0.17	0.10	0.23	0.28	0.15
L	0.73	0.52	0.25	0.50	0.46	0.90	0.56	0.21
I	0.82	0.65	0.35	0.61	0.77	0.75	0.66	0.16
H	0.59	0.38	0.15	0.25	0.67	0.33	0.40	0.18
G	0.62	0.27	0.21	0.19	0.68	0.35	0.39	0.20
F	0.54	0.78	0.32	0.32	0.70	0.23	0.48	0.21
E	0.44	0.21	0.08	0.22	0.61	0.20	0.29	0.18
M	0.62	0.28	0.15	0.53	0.66	0.24	0.41	0.20
Mean	0.58	0.45	0.22	0.37	0.59	0.36		
StDev	0.11	0.17	0.08	0.18	0.18	0.24		

5.1.2. Martindale test - Dark Thermoplastic polyolefin

As can be seen in Table 9 for dark TPO formulations on average TPO1 performs better than the other TPO formulations. This observation is further supported by the fact that the standard deviation of the baseline material is the lowest value. TPO4 and TPO2 show the worst performances as indicated by the fact that they have the highest average value and standard deviation. It can also be seen that the textures *C, B, A* and *M* have overall good performances on TPO formulations.

Table 9. Martindale test - Dark thermoplastic polyolefin ΔE^* values.

Martindale test – Dark thermoplastic polyolefin - ΔE^* values								
Material Texture	TPO5	TPO4	TPO3	TPO2	TPO1	TPO	Average	StDev
D	0.43	1.27	0.64	0.66	0.11	0.39	0.59	0.36
C	0.52	0.33	0.24	0.31	0.12	0.21	0.29	0.13
B	0.35	0.26	0.14	0.25	0.05	0.30	0.22	0.10
A	0.11	0.57	0.02	0.28	0.17	0.12	0.21	0.18
L	0.44	0.08	0.38	0.50	0.29	0.21	0.32	0.14
I	0.22	0.23	0.50	0.46	0.22	0.19	0.31	0.12
H	0.38	0.38	0.39	0.43	0.34	0.15	0.34	0.09
G	0.35	0.57	0.49	0.41	0.80	0.22	0.47	0.18
F	0.46	0.17	0.11	0.16	0.20	0.55	0.28	0.17
E	0.60	0.23	0.38	1.04	0.05	0.31	0.43	0.32
M	0.48	0.36	0.12	0.41	0.05	0.31	0.29	0.16
Mean	0.39	0.40	0.31	0.45	0.22	0.27		
StDev	0.14	0.33	0.20	0.24	0.22	0.12		

5.1.3 Martindale test - Dark Polyamide

As can be seen in Table 10 for dark PA formulations the baseline material shows the worst performances as indicated by both the average value of color difference and standard deviation. PA2 could be considered the best PA formulation because of its lowest average value, yet its standard deviation is higher than that of PA1. Further tests could lead to more accurate conclusions. It can also be seen that *G*, *F* and *E* have overall good performances on PA formulations.

Table 10. Martindale test - Dark polyamide ΔE^* values.

Martindale test – Dark polyamide - ΔE^* values					
Material \ Texture	PA1	PA2	PA6	Average	StDev
D	1.78	1.45	2.05	1.76	0.25
C	1.74	1.85	2.04	1.88	0.12
B	2.01	1.57	2.43	2.01	0.35
A	1.82	1.85	2.10	1.92	0.12
L	2.01	2.00	1.57	1.86	0.21
I	1.54	2.22	1.68	1.81	0.29
H	2.11	1.78	1.86	1.92	0.14
G	1.95	1.80	1.77	1.84	0.08
F	1.93	1.71	1.52	1.72	0.17
E	1.82	1.78	1.81	1.80	0.02
M	2.00	1.57	1.98	1.85	0.20
Mean	1.88	1.78	1.89		
StDev	0.16	0.21	0.26		

5.1.4 Martindale test - Light Polypropylene

As can be seen in Table 11 the baseline polypropylene is the best performing formulation while PP1 and PP5 the worst ones, as in the case of the dark specimens. The textures B, F and M show the lowest average color difference and low values of standard deviation.

Table 11. Martindale test - Light polypropylene ΔE^* values.

Martindale test – Light polypropylene - ΔE^* values								
Material Texture	PP5	PP4	PP3	PP2	PP1	PP	Average	StDev
D	2.36	2.22		1.96	2.86	1.94	2.27	0.33
C	2.16	1.97		2.07	2.40	1.72	2.06	0.23
B	1.85	1.77		2.04	1.92	2.10	1.94	0.12
A	2.26	2.12		2.28	2.12	2.11	2.18	0.08
L	2.34	2.13		2.01	2.08	1.89	2.09	0.15
I	2.70	2.38		2.45	1.95	2.17	2.33	0.25
H	2.20	1.97		2.21	3.21	2.15	2.35	0.44
G	2.31	2.18		2.03	1.91	1.94	2.08	0.15
F	2.19	1.82		1.99	2.10	1.70	1.96	0.18
E	2.10	2.21		2.33	1.84	1.84	2.06	0.20
M	1.88	1.63		1.69	2.14	2.14	1.90	0.21
Mean	2.21	2.04		2.10	2.23	1.97		
StDev	0.23	0.23		0.21	0.43	0.17		

5.1.5 Martindale test - Light Thermoplastic polyolefin

As can be seen in Table 12 the baseline formulation and the TPO5 have the best performance while TPO1 and TPO2 the worst in terms of both average value and standard deviation. Furthermore, it can be observed that the textures *E, F, C, D, I* and *L* have consistent and good performances over all TPO formulations.

Table 12. Martindale test - Light thermoplastic polyolefin ΔE^* values.

Martindale test – Light thermoplastic polyolefin - ΔE^* values								
Material Texture	TPO5	TPO4	TPO3	TPO2	TPO1	TPO	Average	StDev
D	1.89	2.01		1.47	1.04	1.64	1.61	0.34
C	1.80	1.32		1.44	1.35	1.61	1.50	0.18
B	1.63	1.82		1.89	3.03	1.87	2.05	0.50
A	1.79	1.53		1.91	2.80	1.62	1.93	0.45
L	1.32	1.50		2.08	1.93	1.68	1.70	0.28
I	1.47	1.95		2.04	2.13	1.80	1.88	0.23
H	1.90	2.18		1.69	2.05	1.15	1.79	0.36
G	1.85	2.65		1.35	2.20	1.86	1.98	0.43
F	1.52	2.24		3.22	2.33	1.71	2.20	0.60
E	1.68	2.46		3.45	2.14	1.65	2.28	0.66
M	1.45	2.25		1.66	2.63	1.58	1.91	0.45
Mean	1.66	1.99		2.02	2.15	1.65		
StDev	0.20	0.42		0.70	0.58	0.19		

5.1.6 Martindale test - Light Polyamide

The values of the average and standard deviation of the different PA formulations are very similar, therefore it is difficult to state which one is performing the best. It can be seen that the baseline PA features the lowest standard deviation and a color difference value in between the PA1 and PA2, therefore we can assume that it is the best one. Furthermore, it can be seen that the textures *A*, *B*, *I*, *L* have the overall lowest performances on PA formulations while *G*, *E*, *F* and *M* have a consistent and good performance over all the material formulations. This must be further investigated with future tests since PA1 with *B* texture is the best performing specimen while PA6 with texture *D* is among the worst performing.

Table 13. Martindale test - Light polyamide ΔE^* values.

Martindale test - Light polyamide ΔE^* values.					
Material \ Texture	PA1	PA2	PA6	Average	StDev
D	2.16	2.57	3.28	2.67	0.46
C	2.33	2.17	2.77	2.42	0.26
B	2.36	3.24	2.98	2.86	0.37
A	3.13	3.11	2.75	3.00	0.18
L	3.43	3.47	3.22	3.37	0.11
I	3.11	3.14	2.70	2.98	0.20
H	3.05	3.24	2.91	3.07	0.14
G	2.86	2.87	2.75	2.83	0.05
F	2.61	2.48	2.56	2.55	0.06
E	2.68	2.72	2.63	2.68	0.04
M	2.93	2.96	2.74	2.88	0.10
Mean	2.78	2.91	2.85		
StDev	0.39	0.39	0.23		

5.1.7 Martindale – Comparison between white and dark specimens

In the following a comparison of the data of each polymer class (PP, TPO, PA) will be performed in order to see if there are any similarities between dark and light formulations.

Comparison between polypropylene formulations

As can be seen in Table 8 and Table 11 for both formulations PP2 and PP are among the best performing specimens and PP4 and PP5 among the worst specimens. It can also be observed that there is not consistency in the performances of the textures, as the ones that show the lowest ΔE^* for the dark polypropylene do not match with the textures that perform well on the light polypropylene.

Comparison between thermoplastic polyolefin formulations

As can be inferred from Table 9 and Table 12 there best performing dark formulations are TPO1, TPO and TPO3 while the best performing white formulations are TPO and TPO5. The worst performing dark formulations are TPO4 and TPO2 while the worst light formulations are TPO2 and TPO1. Hence Martindale test does not show any similarities between the dark and light specimens. By observing the highest and the lowest ΔE^* of the textures we can see that also in this case there are no similarities between the light and the dark formulations.

Comparison between polyamide formulations

The Martindale test shows a very little discrepancies between the polyamide formulations on both colors for both average value of color difference and standard deviation as can be seen in Table 10 and Table 13. Hence it is difficult to state which formulation is performing the best. On the other hand it can be observed that on average the textures *E* and *F* are the best performing in both color formulations.

5.1.8 Martindale test – Formulation comparison

Martindale test results in Figure 53 and Figure 54 shown that for both dark and light formulations PA1, PA2 and PA6 values are higher than those of the other polymers. In order to identify what formulations are performing from the resistance to soiling point of view the best the average ΔE^* for each class has been considered as in Table 14 where a color scale from red (maximum) to green (minimum) has been adopted for an easier data interpretation.

It can be observed that on average thermoplastic polyolefins have lower values of ΔE^* than the polypropylenes, which means that the latter have higher propensity to soiling than the former. It is also shown in Table 14 that, ignoring PP3 which comes just in the dark color, the best performing polypropylene formulations are the baseline and PP2 and PP4. The best performing thermoplastic polyolefins formulations excluding TPO3 (it comes just in the dark color) are the baseline and TPO1. On the other hand the it is impossible to state which polyamide formulation shows less propensity to soiling because their values of ΔE^* are very close to each other.

Furthermore, it can be observed that the spread (ΔE^* max-min) of the dark formulations values is higher than that of the light formulations and this is in agreement with the visual observations. During the tests all the light coupons had a visible black path on them while it was sometimes almost impossible to spot on the dark coupons.

Table 14 .Martindale - Average ΔE^* of each polymer formulation.

	Martindale test - ΔE^* mean	
	Dark	Light
PP	0.36	1.97
PP1	0.59	2.23
PP2	0.37	2.10
PP3	0.22	
PP4	0.45	2.04
PP5	0.58	2.21
TPO	0.27	1.65
TPO1	0.22	2.15
TPO2	0.45	2.02
TPO3	0.31	
TPO4	0.40	1.99
TPO5	0.39	1.66
PA6	1.89	2.80
PA1	1.88	2.78
PA2	1.78	2.91
ΔE^* max-min	1.67	1.26

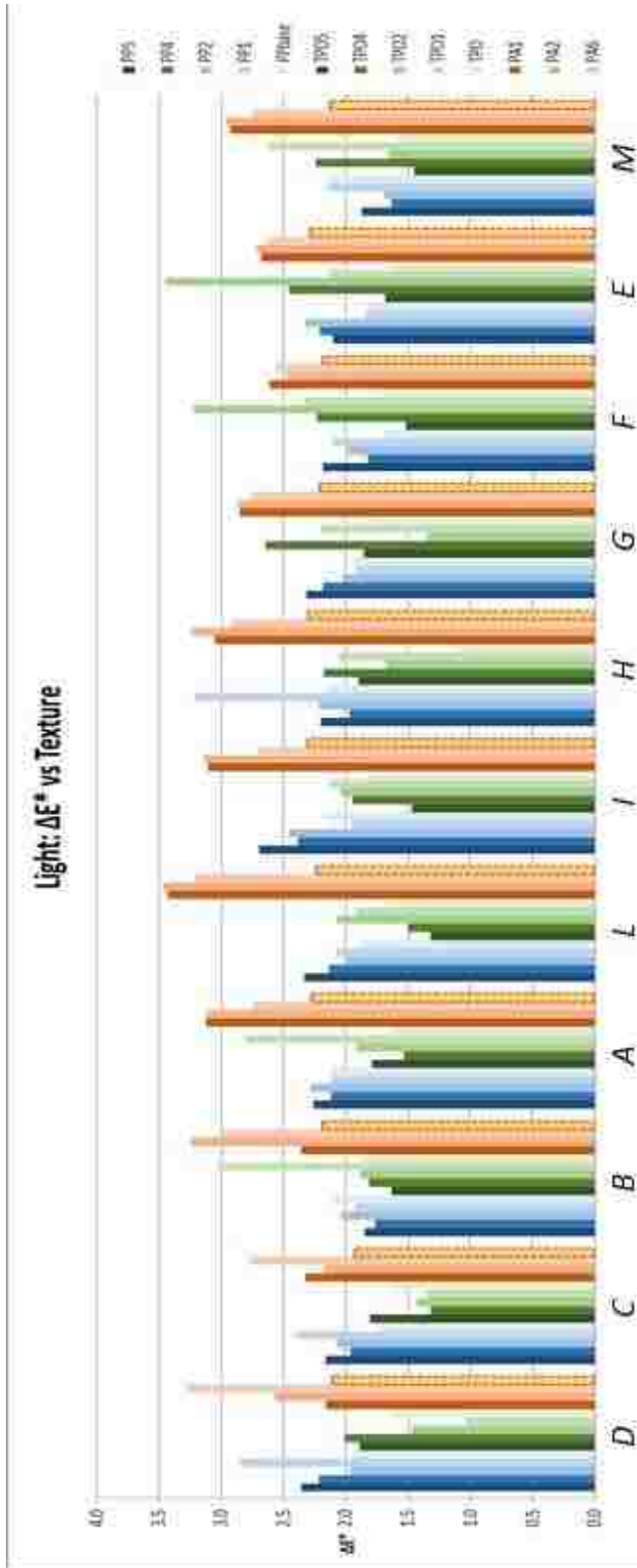


Figure 53. Martindale - Light: ΔE^* vs Texture.

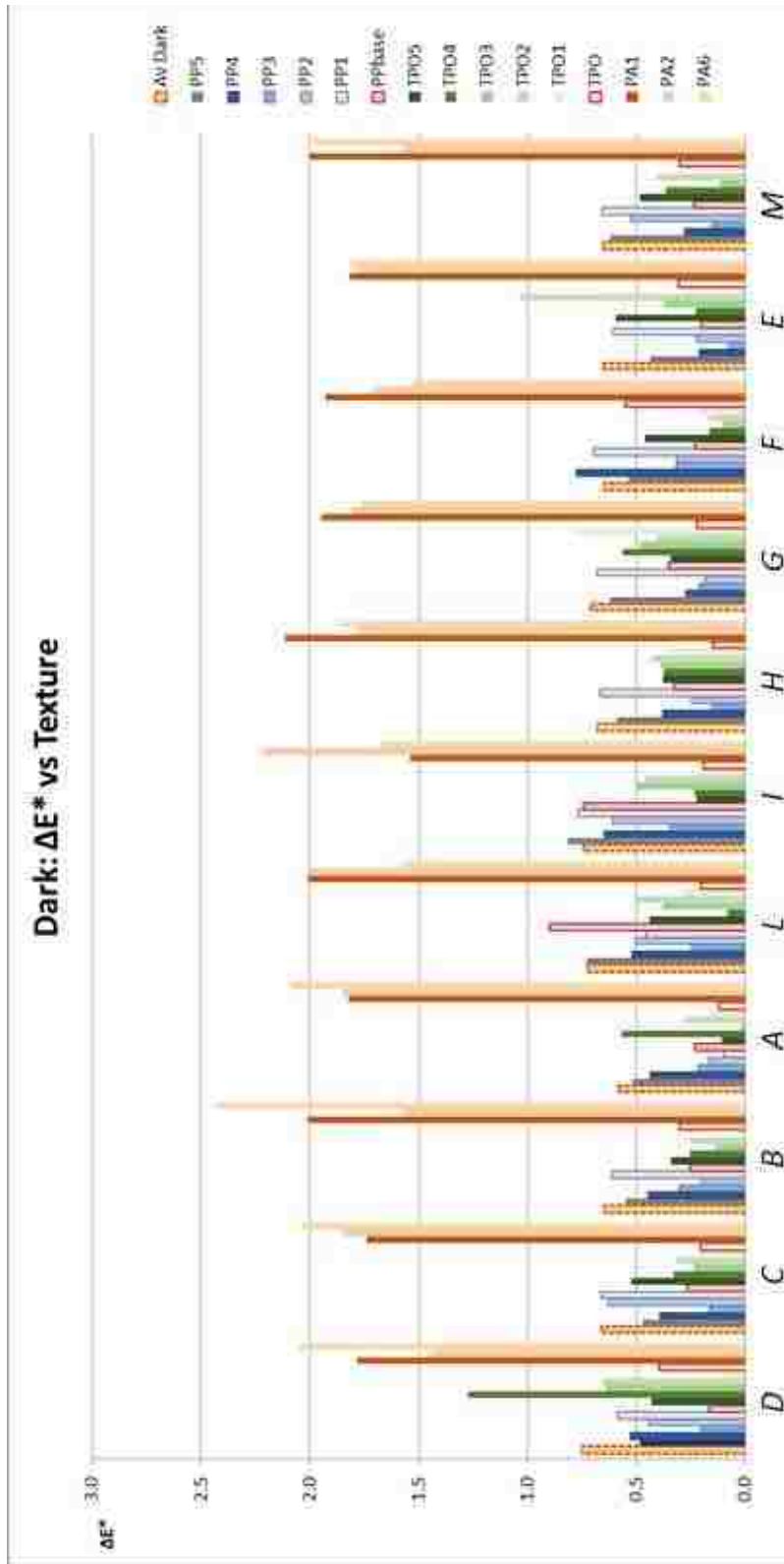


Figure 54. Martindale - Dark: ΔE^* vs Texture.

5.2 Martindale test - Texture effect

Martindale test results organized in order to show the effect of each texture formulation are shown in Figure 55 and Figure 56. As can be seen the results are quite scattered therefore, the average value of the ΔE^* for each texture is considered for further analysis. As can be seen in Table 15 the textures *A*, *B* and *M* are among the best performing textures on both light and dark formulations while the textures *I*, *D*, *G* and *H* are among the worst.

Furthermore, the ΔE^* max-min values are much lower than in the case of the materials. Hence the effect of the texture is lower than that of the materials because the differences among texture values are lower than the differences among the material values.

Table 15. Martindale -Average ΔE^* of each texture.

Texture	Martindale test - ΔE^* mean	
	Dark	Light
F	0.65	2.19
M	0.65	2.13
D	0.75	2.28
H	0.68	2.30
L	0.72	2.24
B	0.65	1.98
E	0.65	2.29
C	0.66	2.09
G	0.71	2.21
I	0.75	2.31
A	0.58	2.11
ΔE^* max-min	0.17	0.33

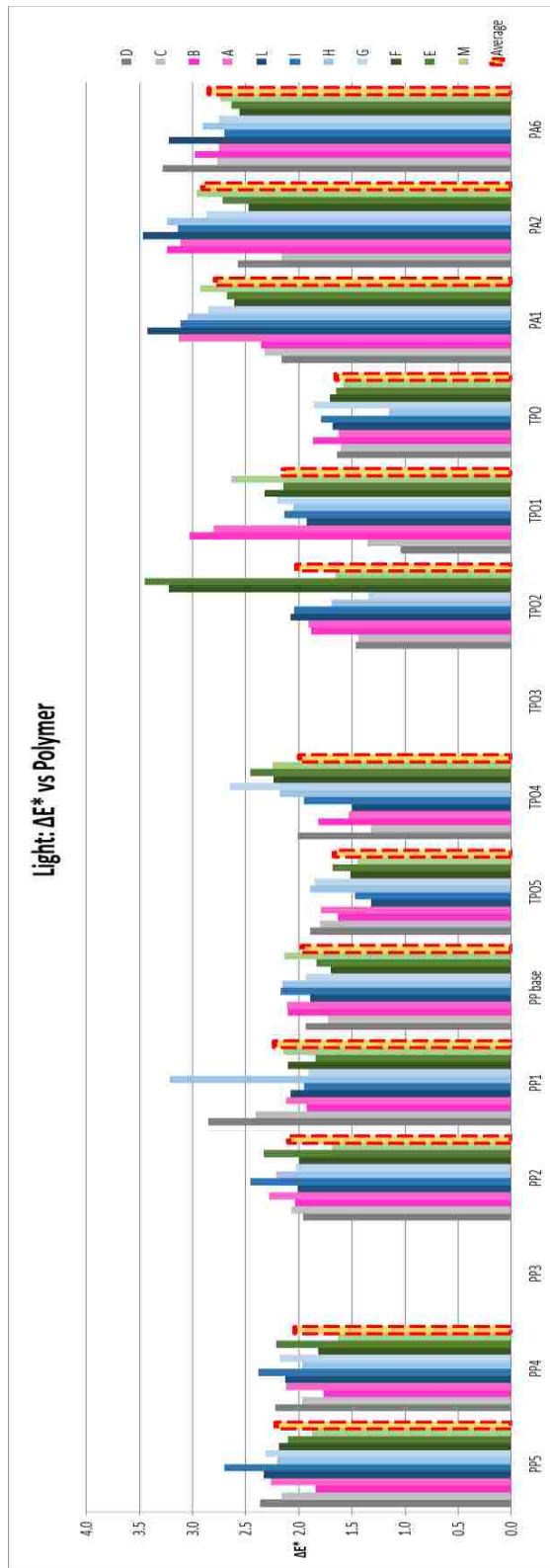


Figure 55. Martindale - Light: ΔE^* vs Polymer.

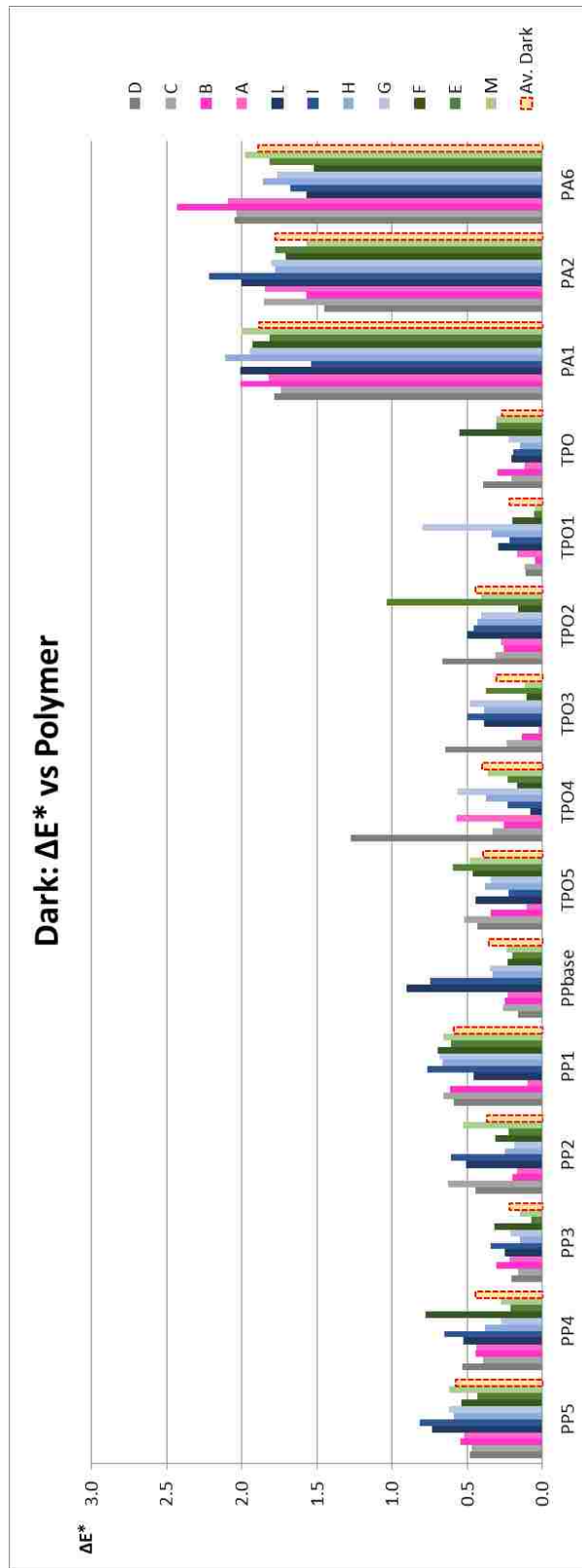


Figure 56. Martindale - Dark: ΔE^* vs Polymer.

5.3 Dusting test – Material effect

5.3.1 Dusting test - Dark Polypropylene

Dusting test showed dark PP baseline performs considerably better than the other formulations while PP4 and PP2 considerably worse, as can be seen in Table 16. It can also be observed that the best performing textures are *A*, *B* and *F*.

Table 16. Dusting test - Dark polypropylene ΔE^* values.

		Dusting test - Dark polypropylene - ΔE^* values						
Material Texture	PP5	PP4	PP3	PP2	PP1	PP	Average	StDev
<i>D</i>	0.85	0.83	1.01	0.64	0.61	0.64	0.76	0.15
<i>C</i>	0.51	0.89	0.67	0.67	0.68	0.22	0.61	0.20
<i>B</i>	0.22	0.45	0.13	0.36	0.47	0.34	0.33	0.12
<i>A</i>	0.08	0.27	0.23	0.49	0.11	0.18	0.23	0.13
<i>L</i>	0.79	1.06	0.63	1.02	0.88	0.70	0.85	0.16
<i>I</i>	0.21	0.56	0.29	0.67	0.29	0.08	0.35	0.20
<i>H</i>	1.11	0.98	1.28	1.30	1.10	0.87	1.11	0.15
<i>G</i>	0.57	0.95	0.70	0.85	0.28	0.53	0.65	0.22
<i>F</i>	0.63	0.71	0.36	0.56	0.43	0.40	0.51	0.13
<i>E</i>	0.31	1.06	0.50	0.53	0.16	0.15	0.45	0.31
<i>M</i>	0.80	0.90	0.38	0.60	0.57	0.23	0.58	0.23
Average	0.55	0.79	0.56	0.70	0.51	0.40		
StDev	0.32	0.26	0.35	0.27	0.30	0.26		

5.3.2 Dusting test - Dark Thermoplastic polyolefin

Dusting test shows that the best formulations are TPO3 and TPO1 as can be seen in Table 17. It is of interest to notice that the top three values are the same for both Martindale and Dusting test. It can also be observed that the best performing textures are *B, I, E, M* and *C*, as in the Martindale test.

Table 17. Dusting test - Dark thermoplastic polyolefin values.

		Dusting test – Dark thermoplastic polyolefin - ΔE^* values						
Material Texture	TPO5	TPO4	TPO3	TPO2	TPO1	TPO	Average	StDev
<i>D</i>	0.63	0.72	0.13	0.57	0.80	0.81	0.61	0.23
<i>C</i>	0.14	0.61	0.16	0.26	0.31	0.08	0.26	0.17
<i>B</i>	0.57	0.29	0.20	0.22	0.42	0.21	0.32	0.14
<i>A</i>	0.65	0.44	0.47	0.43	0.28	0.22	0.42	0.14
<i>L</i>	0.81	0.92	0.35	0.57	0.57	0.48	0.62	0.19
<i>I</i>	0.47	0.23	0.10	0.42	0.38	0.29	0.31	0.12
<i>H</i>	0.78	0.77	0.49	0.90	0.72	0.91	0.76	0.14
<i>G</i>	0.53	0.73	0.44	1.13	0.48	0.45	0.63	0.25
<i>F</i>	0.36	0.62	0.06	0.43	0.21	0.21	0.32	0.18
<i>E</i>	0.25	0.39	0.31	0.26	0.30	0.02	0.26	0.11
<i>M</i>	0.53	0.36	0.10	0.34	0.24	0.37	0.32	0.13
Average	0.52	0.55	0.26	0.50	0.43	0.37		
StDev	0.21	0.22	0.16	0.29	0.20	0.28		

5.3.3 Dusting test - Dark Polyamide

Dusting test showed that the PA2 is performing better than the baseline formulation, while the PA61 is performing worse as can be inferred from Table 18. It is of interest to remark that PA2 was overall better than PA6 and PA1 also according to the Martindale results. It can be observed that the best performing textures are B, L and M.

Table 18. Dusting test - Dark polyamide ΔE^* values.

		Dusting test – Dark polyamide - ΔE^* values				
Material \ Texture	PA1	PA2	PA6	Average	StDev	
<i>D</i>	0.28	0.26	0.39	0.31	0.06	
<i>C</i>	0.92	0.07	0.17	0.39	0.38	
<i>B</i>	0.24	0.27	0.37	0.29	0.06	
<i>A</i>	0.55	0.51	0.33	0.46	0.09	
<i>L</i>	0.17	0.26	0.42	0.28	0.10	
<i>I</i>	0.68	0.10	0.26	0.35	0.25	
<i>H</i>	0.47	0.88	0.30	0.55	0.24	
<i>G</i>	0.95	0.08	0.33	0.45	0.36	
<i>F</i>	0.53	0.45	0.74	0.57	0.12	
<i>E</i>	1.00	0.57	0.33	0.63	0.28	
<i>M</i>	0.41	0.11	0.32	0.28	0.13	
Average	0.56	0.32	0.36			
StDev	0.29	0.26	0.14			

5.3.4 Dusting test - Light Polypropylene

As can be inferred from Table 19 the Dusting test shows that on average PP baseline performs better than the other formulations. PP4 and PP1 could be considered the worst performing formulations. Furthermore, it can be observed that the best performing textures are *B*, *L* and *M* while the worst performing are *E*, *F* and *C*.

Table 19. Dusting test - Light polypropylene ΔE^* values.

		Dusting test - Light polypropylene - ΔE^* values						
Material Texture	PP5	PP4	PP3	PP2	PP1	PP	Average	StDev
<i>D</i>	1.35	1.71		1.46	2.07	1.53	1.62	0.25
<i>C</i>	2.89	2.45		2.81	1.98	1.40	2.31	0.55
<i>B</i>	0.47	1.71		0.92	1.09	0.93	1.03	0.40
<i>A</i>	1.17	3.12		1.08	1.34	1.13	1.57	0.78
<i>L</i>	0.67	1.08		1.56	1.62	1.20	1.22	0.35
<i>I</i>	2.21	2.43		2.79	1.66	1.25	2.07	0.55
<i>H</i>	1.20	1.81		1.98	1.51	1.25	1.55	0.31
<i>G</i>	2.40	2.72		2.95	1.38	1.28	2.15	0.69
<i>F</i>	3.01	2.08		1.50	5.39	3.58	3.11	1.35
<i>E</i>	3.51	3.51		3.11	2.87	2.84	3.17	0.29
<i>M</i>	1.50	1.65		1.01	1.97	1.50	1.53	0.31
Average	1.85	2.21		1.93	2.08	1.63		
StDev	1.01	0.72		0.84	1.20	0.82		

5.3.5 Dusting test – Light Thermoplastic polyolefin

Dusting test shows that TPO baseline on average is performing worse than the other formulations as can be inferred from Table 20. It is difficult to state which one is the best because their performances are strictly related to the textures and it is not possible to identify a pattern too. On average the textures *G*, *I* and *C* are the best performing textures while *D*, *H*, *F* and *E* are the worst.

Table 20. Dusting test - Light thermoplastic polyolefin ΔE^* values.

		Dusting test – Light thermoplastic polyolefin - ΔE^* values						
Material Texture	TPO5	TPO4	TPO3	TPO2	TPO1	TPO	Average	StDev
<i>D</i>	1.33	2.34		3.20	2.22	3.51	2.52	0.77
<i>C</i>	2.29	2.54		0.90	0.88	1.78	1.68	0.69
<i>B</i>	0.23	1.78		1.95	0.69	3.85	1.70	1.26
<i>A</i>	2.81	1.35		1.78	2.11	2.42	2.09	0.51
<i>L</i>	0.22	1.15		2.40	1.81	4.03	1.92	1.28
<i>I</i>	2.47	1.43		0.53	1.63	1.49	1.51	0.62
<i>H</i>	2.03	1.67		3.12	1.88	4.44	2.63	1.04
<i>G</i>	1.36	1.44		0.86	1.26	1.15	1.21	0.20
<i>F</i>	2.73	1.84		3.04	3.09	7.05	3.55	1.81
<i>E</i>	3.79	1.80		2.00	2.54	3.53	2.73	0.80
<i>M</i>	1.77	2.44		0.95	2.41	3.03	2.12	0.71
Average	1.91	1.80		1.88	1.87	3.30		
StDev	1.09	0.47		0.98	0.72	1.65		

5.3.6 Dusting test – Light polyamide

The Dusting test shows that both PA1 and PA2 are performing better than the PA6 as shown in Table 21. Furthermore, PA2 is the best performing formulation. It can also be observed that *D*, *A*, *E*, *F* and *CMP M* are the best performing textures while *C*, *D* and *G* are the worst.

Table 21. Dusting test - Light polyamide ΔE^* values.

		Dusting test – Light polyamide - ΔE^* values				
Material \ Texture	PA1	PA2	PA6	Average	StDev	
<i>D</i>	0.51	0.90	1.77	1.06	0.53	
<i>C</i>	1.23	0.87	4.47	2.19	1.62	
<i>B</i>	3.07	0.94	1.13	1.72	0.96	
<i>A</i>	1.33	0.82	1.51	1.22	0.29	
<i>L</i>	2.41	0.96	1.58	1.65	0.60	
<i>I</i>	1.40	0.94	2.32	1.56	0.58	
<i>H</i>	2.24	1.05	2.14	1.81	0.54	
<i>G</i>	1.07	1.47	2.85	1.80	0.76	
<i>F</i>	0.31	0.75	1.84	0.97	0.64	
<i>E</i>	0.67	0.96	1.45	1.03	0.32	
<i>M</i>	0.69	0.48	1.69	0.96	0.53	
Average	1.36	0.92	2.07			
StDev	0.88	0.24	0.92			

5.3.7 Dusting test – Comparison between white and dark specimens

In the following a comparison of the data of each polymer class (PP, TPO, PA) will be performed in order to see if there are any similarities between dark and light formulations.

Comparison between polypropylene formulations

As can be seen in Table 16 and Table 19, for both formulations PP is the best performing formulation and PP4 the worst performing formulation. No similarities are observed for what concerns the textures.

Comparison between thermoplastic polyolefin formulations

As can be inferred from Table 17 and Table 20 there are no similarities between dark and light formulations. On the contrary a polymer that performs well in one color does not do the same in the other. Some examples are TPO that is performing well in the dark formulation and bad in the light one, or TPO4 which is showing an opposite trend. No similarities were observed in the performances of the textures either.

Comparison between polyamide formulations

The Dusting test shows that PA2 performs the best in both color formulations. Textures performances are quite scattered and it is not possible to observe any similarities between dark and light specimens.

5.3.8 Dusting test – Formulations comparison

Dusting test results organized in order to show the effect of each polymer formulation are shown in Figure 57 and Figure 58. It can be observed that the values of PA1, PA2 and PA6 are not the worst ones as in the Martindale test. As can be seen in Table 22, PP and PA2 perform well in both color formulations while PP4, PP2 and TPO4 can be considered the worst performing.

Table 22. Dusting - Average ΔE^* of each polymer formulation.

	Dusting test - ΔE^* mean	
	Dark	Light
PP	0.40	1.63
PP1	0.51	2.08
PP2	0.70	1.93
PP3	0.56	
PP4	0.79	2.21
PP5	0.55	1.85
TPO	0.37	3.30
TPO1	0.43	1.87
TPO2	0.50	1.88
TPO3	0.26	
TPO4	0.55	1.80
TPO5	0.52	1.91
PA6	0.36	2.07
PA1	0.56	1.36
PA2	0.32	0.92
ΔE^* max-min	0.53	2.38

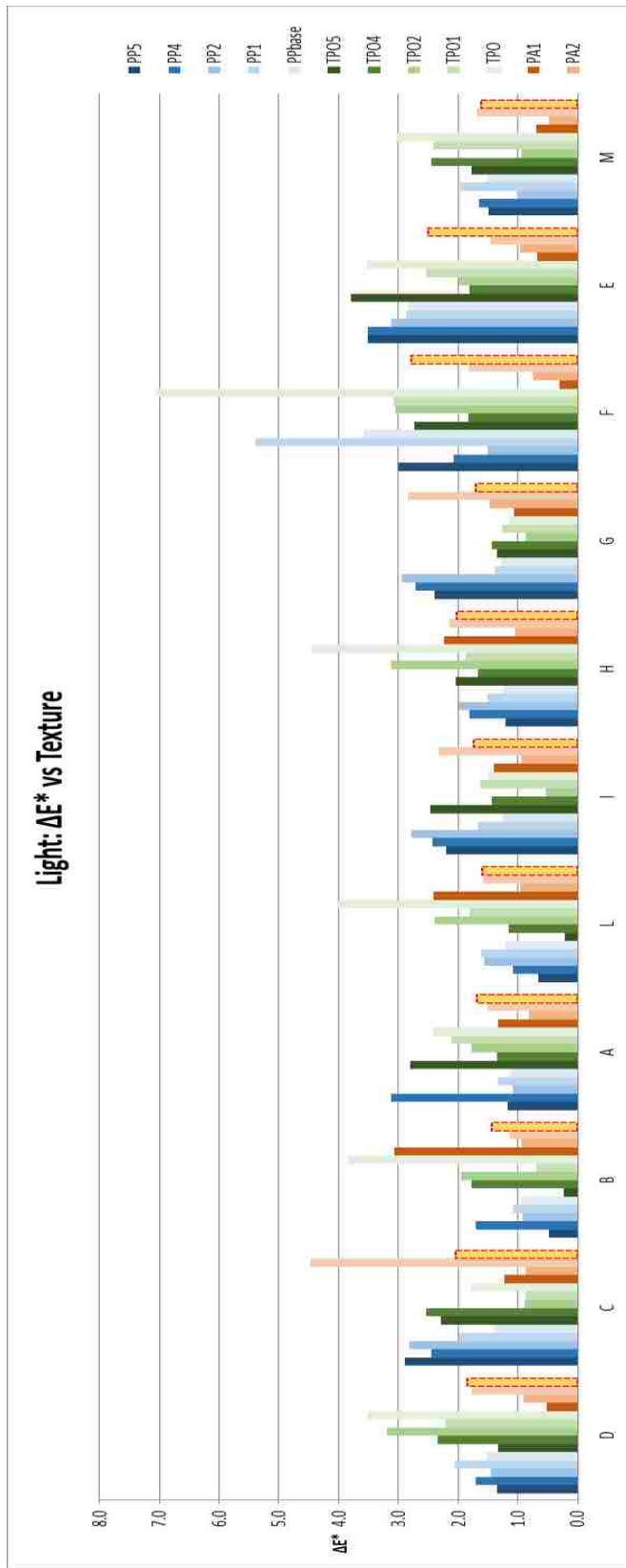


Figure 57. Dusting - Light: ΔE^* vs Texture.

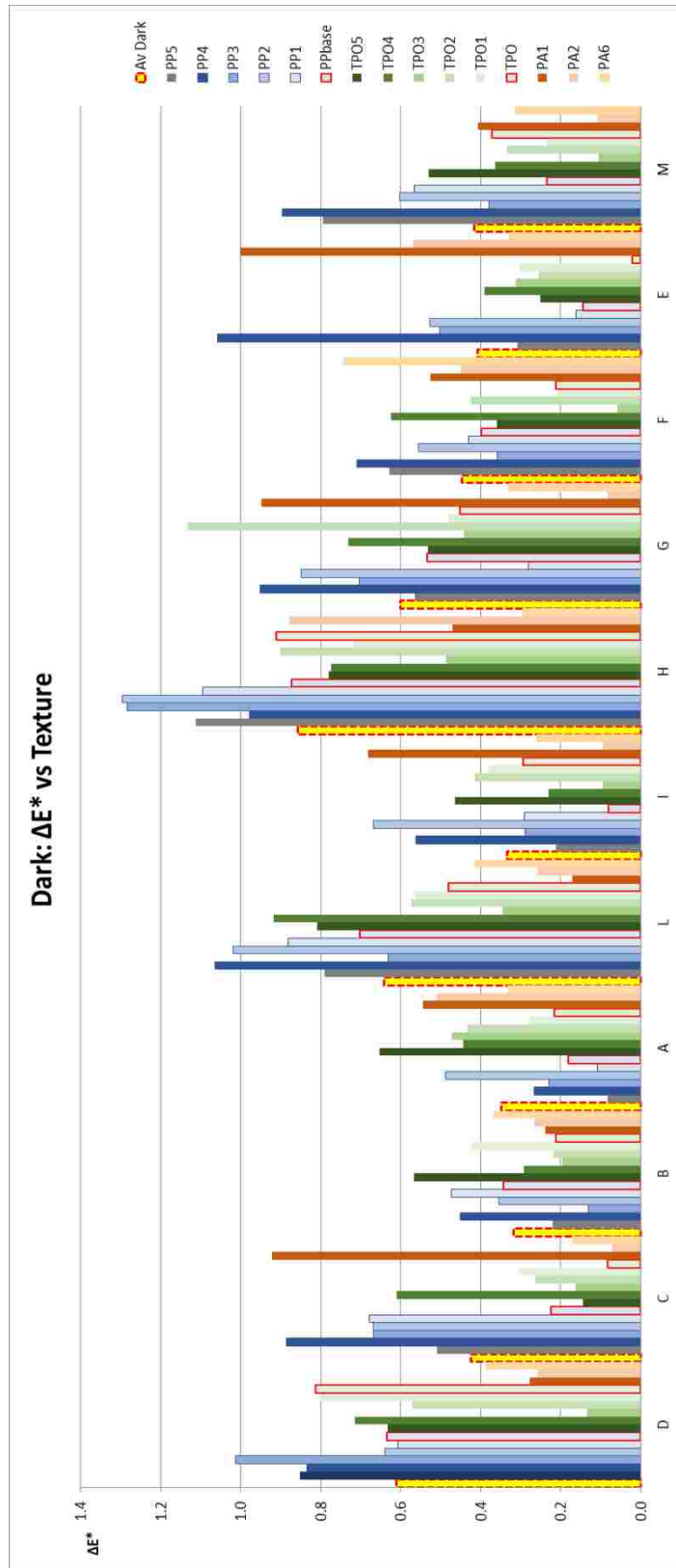


Figure 58. Dusting -Dark: ΔE^* vs Texture.

5.4 Dusting test - Texture effect

Dusting test results organized in order to show the effect of each texture formulation are shown in Figure 59 and Figure 60. It can be seen that *A* and *B* show the best compromise while *G*, *E* and *D* can be considered the worst textures. It must be mentioned that as for the other test methodologies there are not any similarities between the performances of the dark and light specimens.

Furthermore, the values of ΔE^* max min of Table 22 and Table 23 show that the effect of the textures and of the materials on the propensity to soiling are similar in the dusting test.

Table 23. Dusting - Average ΔE^* of each texture.

Texture	Dusting test - ΔE^* mean	
	Dark	Light
F	0.45	2.78
M	0.42	1.62
D	0.61	1.84
H	0.86	2.03
L	0.64	1.59
B	0.32	1.44
E	0.41	2.51
C	0.42	2.04
G	0.60	1.71
I	0.33	1.74
A	0.35	1.69
ΔE^* max-min	0.54	1.34

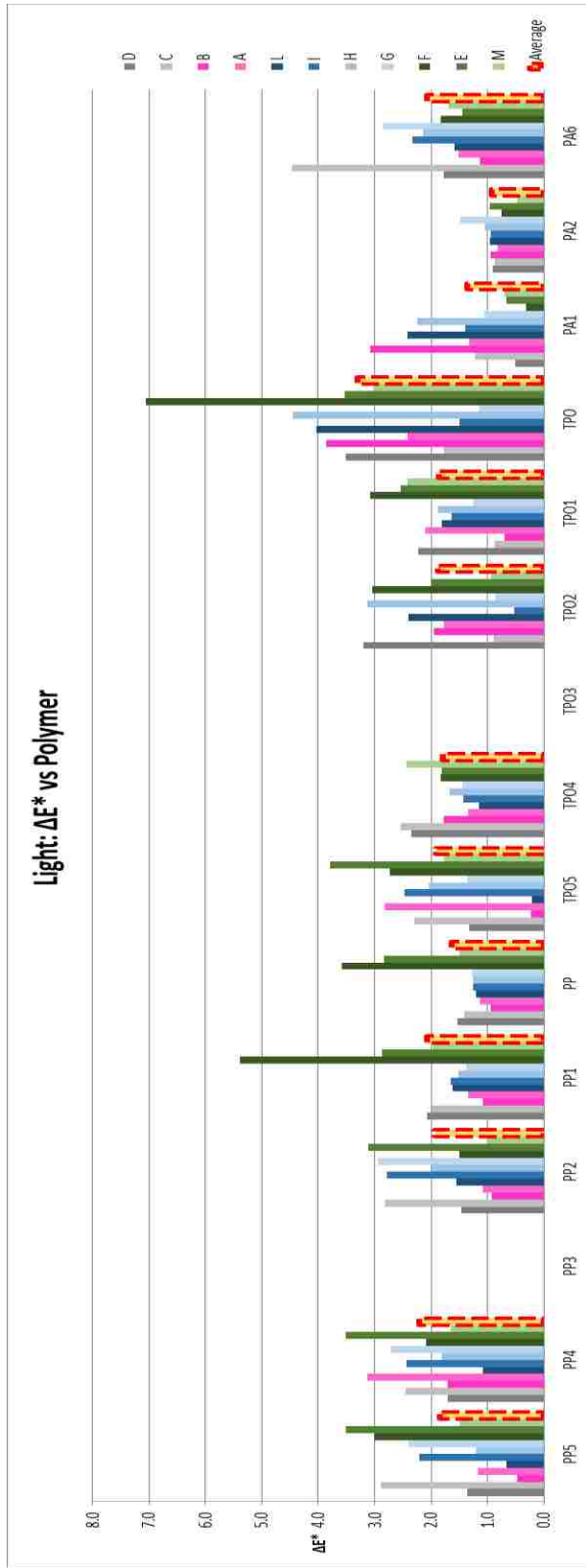


Figure 59. Dusting - Light: ΔE^* vs Polymer.

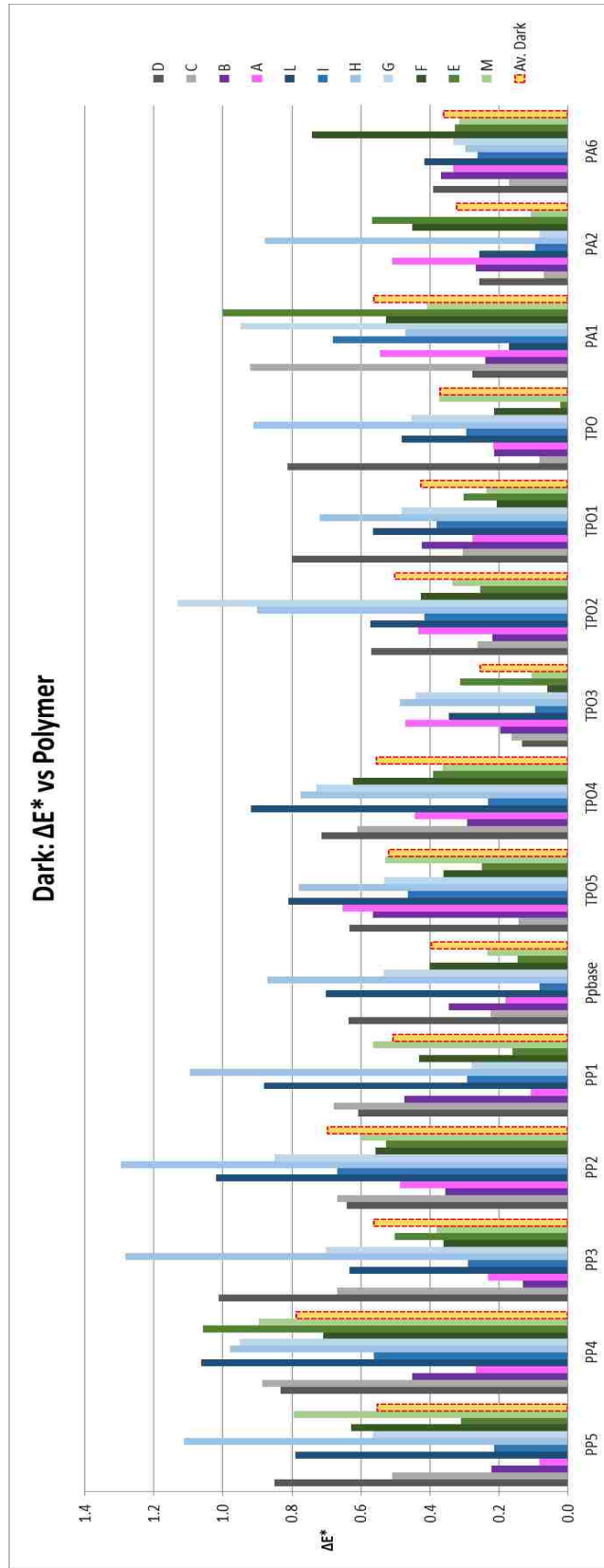


Figure 60. Dusting - Dark: ΔE^* vs Polymer.

5.5 Fingerprint test – Material effect

5.5.1 Fingerprint test - Dark Polypropylene

Fingerprint test shows that PP baseline is performing better than the other formulations. It can also be observed that PP4 and PP3 show similar performances to the baseline formulation. The best performing textures are *D*, *A* and *M* while *C*, *B* and *I* are the worst as can be inferred from Table 24.

Table 24. Fingerprint test - Dark polypropylene ΔE^* values.

		Fingerprint test - Dark polypropylene - ΔE^* values						
Material \ Texture	PP5	PP4	PP3	PP2	PP1	PP	Average	StDev
<i>D</i>	0.70	0.17	0.49	0.44	0.53	0.68	0.50	0.18
<i>C</i>	1.16	0.91	1.30	0.81	0.45	0.81	0.91	0.27
<i>B</i>	0.77	0.70	0.81	0.74	1.61	0.57	0.87	0.34
<i>A</i>	1.04	0.62	0.47	0.29	1.13	0.35	0.65	0.33
<i>L</i>	0.92	0.70	0.27	1.00	1.18	0.33	0.73	0.34
<i>I</i>	1.03	0.95	0.41	0.90	1.56	0.41	0.88	0.39
<i>H</i>	1.37	0.44	0.15	0.09	0.76	0.39	0.53	0.43
<i>G</i>	0.64	1.04	0.82	1.06	0.53	0.98	0.85	0.20
<i>F</i>	1.07	0.47	0.71	0.96	0.95	0.54	0.78	0.23
<i>E</i>	1.30	0.63	0.60	0.85	0.82	0.73	0.82	0.23
<i>M</i>	1.01	0.54	0.80	0.64	0.67	0.53	0.70	0.17
Average	1.00	0.65	0.62	0.71	0.93	0.57		
StDev	0.23	0.25	0.32	0.31	0.40	0.21		

5.5.2 Fingerprint test - Dark Thermoplastic polyolefin

Fingerprint test shows that TPO3 is performing better than the other formulations and that TPO5, TPO3 and TPO1 perform better than the baseline as can be inferred from Table 25. It can also be observed that the best performing textures are *D*, *F* and *M*, while *C*, *I* and *G* are the worst.

Table 25. Fingerprint test - Dark thermoplastic polyolefin ΔE^* values.

		Fingerprint test – Dark thermoplastic polyolefin - ΔE^* values						
Material \ Texture	TPO5	TPO4	TPO3	TPO2	TPO1	TPO	Average	StDev
<i>D</i>	0.23	0.36	0.31	0.19	0.04	0.18	0.22	0.10
<i>C</i>	0.49	0.72	0.16	0.67	0.39	0.63	0.51	0.19
<i>B</i>	0.26	0.58	0.16	0.60	0.19	0.65	0.41	0.21
<i>A</i>	0.31	0.87	0.18	0.60	0.53	0.22	0.45	0.24
<i>L</i>	0.10	0.31	0.37	0.64	0.30	0.17	0.32	0.17
<i>I</i>	0.36	0.57	0.29	0.71	0.56	0.51	0.50	0.14
<i>H</i>	0.03	0.45	0.22	0.04	0.10	0.53	0.23	0.20
<i>G</i>	0.54	0.58	0.28	0.65	0.28	0.81	0.52	0.19
<i>F</i>	0.24	0.37	0.06	0.28	0.13	0.14	0.20	0.10
<i>E</i>	0.36	0.53	0.20	0.18	0.59	0.30	0.36	0.15
<i>M</i>	0.26	0.14	0.26	0.14	0.17	0.07	0.17	0.07
Average	0.29	0.50	0.23	0.43	0.30	0.38		
StDev	0.15	0.20	0.09	0.26	0.20	0.25		

5.5.3 Fingerprint test - Dark Polyamide

The Fingerprint test shows that PA2 performs considerably better than the other formulations and that PA6 is the worst performing formulation as can be inferred from the Table 26. It can also be observed that the best performing textures are *C*, *E* and *M* while *A* and *B* are the worst performing.

Table 26. Fingerprint test - Dark polyamide ΔE^* values.

		Fingerprint test – Dark polyamide - ΔE^* values			
Material Texture	PA1	PA2	PA6	Average	StDev
<i>D</i>	1.31	0.91	2.41	1.54	0.63
<i>C</i>	1.36	1.04	1.76	1.39	0.29
<i>B</i>	2.25	0.81	3.88	2.31	1.25
<i>A</i>	2.45	0.95	2.46	1.95	0.71
<i>L</i>	1.74	0.72	2.64	1.70	0.78
<i>I</i>	1.78	1.05	1.84	1.56	0.36
<i>H</i>	1.93	0.81	2.31	1.68	0.64
<i>G</i>	2.03	0.91	1.72	1.55	0.47
<i>F</i>	0.81	0.48	2.96	1.42	1.10
<i>E</i>	1.30	1.03	1.47	1.27	0.18
<i>M</i>	0.79	0.49	1.73	1.00	0.53
Average	1.61	0.84	2.29		
StDev	0.55	0.20	2.50		

5.5.4 Fingerprint test - Light Polypropylene

The fingerprint test shows that PP baseline is performing worse than the other formulations while PP5 and PP4 are performing the best as referred in Table 27. It can also be observed that the best performing textures are *F*, *E*, *M* and *B* and *G* are the worst.

Table 27. Fingerprint test - Light polypropylene ΔE^* values.

		Fingerprint test - Light polypropylene - ΔE^* values						
Material Texture	PP5	PP4	PP3	PP2	PP1	PP	Average	StDev
<i>D</i>	1.64	1.57		2.06	2.31	2.97	2.11	0.51
<i>C</i>	1.81	1.96		2.05	2.59	2.21	2.12	0.27
<i>B</i>	2.42	1.20		2.67	1.79	4.49	2.51	1.11
<i>A</i>	2.81	1.87		1.60	2.84	1.02	2.03	0.71
<i>L</i>	1.34	1.83		2.34	2.51	2.39	2.08	0.44
<i>I</i>	1.02	1.60		2.50	2.27	2.84	2.05	0.65
<i>H</i>	1.21	1.78		2.12	2.86	2.26	2.05	0.54
<i>G</i>	1.81	1.91		1.59	3.33	2.69	2.27	0.65
<i>F</i>	0.48	2.41		1.57	1.81	1.52	1.56	0.62
<i>E</i>	0.96	2.04		2.14	1.81	1.67	1.72	0.42
<i>M</i>	1.85	0.57		1.77	1.35	2.43	1.59	0.62
Average	1.58	1.70		2.04	2.32	2.41		
StDev	0.67	0.48		0.38	0.59	0.91		

5.5.5 Fingerprint test - Light Thermoplastic polyolefin

As can be observed in Table 28 the fingerprint test shows that TPO1 and TPO baseline are the best performing formulations and that TPO5 is the worst performing formulation. It can also be observed that the best performing formulation is *L* while *D* and *B* are the worst formulations.

Table 28. Fingerprint test - Light thermoplastic polyolefin ΔE^* values.

		Fingerprint test – Light thermoplastic polyolefin - ΔE^* values						
Material Texture	TPO5	TPO4	TPO3	TPO2	TPO1	TPO	Average	StDev
<i>D</i>	3.25	2.13		4.10	3.60	2.26	3.07	0.76
<i>C</i>	3.58	3.51		1.77	2.94	2.58	2.88	0.67
<i>B</i>	3.34	3.57		1.80	3.21	3.30	3.04	0.63
<i>A</i>	2.34	4.15		2.87	0.42	2.54	2.46	1.20
<i>L</i>	2.33	3.54		2.94	2.00	2.56	2.67	0.53
<i>I</i>	3.05	2.60		3.77	3.13	0.63	2.64	1.07
<i>H</i>	3.41	3.17		2.85	2.95	2.44	2.96	0.33
<i>G</i>	3.50	1.61		3.46	3.31	2.98	2.97	0.71
<i>F</i>	3.65	3.22		2.16	1.71	2.98	2.74	0.71
<i>E</i>	4.46	2.26		3.12	1.55	1.54	2.59	1.10
<i>M</i>	2.88	2.69		3.17	2.67	3.55	2.99	0.33
Average	3.25	2.95		2.91	2.50	2.49		
StDev	0.61	0.76		0.75	0.96	0.82		

5.5.6 Fingerprint test - Light Polyamide

As can be observed in Table 29 fingerprint test shows that the PA2 is the best performing formulation even though PA6 values are similar. It can be observed that PA1 is performing much worse than PA2 and PA6. As can be seen from the Table 29, the texture *D* is the worst performing texture while it is difficult to draw conclusions for what regards the best values because low value of the average are related to high values of the standard deviation.

Table 29. Fingerprint test - Light polyamide ΔE^* values.

		Fingerprint test – Light polyamide - ΔE^* values				
Material \ Texture	PA1	PA2	PA6	Average	StDev	
<i>D</i>	6.32	3.20	2.95	4.16	1.53	
<i>C</i>	4.64	2.57	0.99	2.73	1.49	
<i>B</i>	3.52	1.79	2.62	2.64	0.71	
<i>A</i>	2.46	4.33	2.36	3.05	0.91	
<i>L</i>	3.75	1.78	1.59	2.37	0.98	
<i>I</i>	2.28	2.50	2.86	2.55	0.24	
<i>H</i>	4.98	2.39	2.75	3.37	1.15	
<i>G</i>	1.72	1.10	3.84	2.22	1.17	
<i>F</i>	3.50	3.25	2.62	3.12	0.37	
<i>E</i>	4.27	2.44	2.65	3.12	0.82	
<i>M</i>	2.22	2.29	3.53	2.68	0.60	
Average	3.61	2.51	2.61			
StDev	1.39	0.86	0.79			

5.5.7 Fingerprint test – Comparison between white and dark specimens

In the following a comparison of the data of each polymer class (PP, TPO, PA) will be performed in order to see if there are any similarities between dark and light formulations. The top and bottom three values have usually been reported. Two values instead of three are shown when they are significantly different from the others.

Comparison between polypropylene formulations

Fingerprint test shows no similarity between the performances of the white and black formulations as can be inferred from Table 24 and Table 27. It can also be observed that no correlation occurs between the textures performances. On the contrary the texture *D* is performing well on light formulations and bad on dark formulations.

Comparison between thermoplastic polyolefin formulations

As can be inferred from Table 25 and Table 28 thermoplastic polyolefin do not show any similarities neither among the textures nor among the polymer formulations in both colors.

Comparison between polyamide formulations

The Fingerprint test shows that PA2 performs the best in both color formulations. Textures performances are quite scattered and it is not possible to observe any similarities between dark and light specimens. On the contrary, the textures *E* and *F* perform well on the dark specimens and bad on the light specimens.

5.5.8 Fingerprint test – Formulations comparison

Fingerprint test results organized in order to show the effect of each polymer formulation are shown in Figure 61 and Figure 62. It can be seen that PA6, PA1 and PA2 have high values of color difference and that on average dark thermoplastic polyolefin formulations perform better than dark polypropylene formulation. As can be also inferred from the average ΔE^* of Table 30 the opposite holds for light formulations. Average ΔE^* spread is similar for both dark and light specimens therefore, the contrast between the colors and the soiling agent is not influencing the results.

Table 30. Fingerprint - Average ΔE^* of each polymer formulation.

	Fingerprint test - ΔE^* mean	
	Dark	Light
PP	0.57	2.41
PP1	0.93	2.32
PP2	0.71	2.04
PP3	0.62	
PP4	0.65	1.70
PP5	1.00	1.58
TPO	0.38	2.49
TPO1	0.30	2.50
TPO2	0.43	2.91
TPO3	0.23	
TPO4	0.50	2.95
TPO5	0.29	3.25
PA6	2.29	2.61
PA1	1.61	3.61
PA2	0.84	2.51
ΔE^* max-min	2.06	2.03

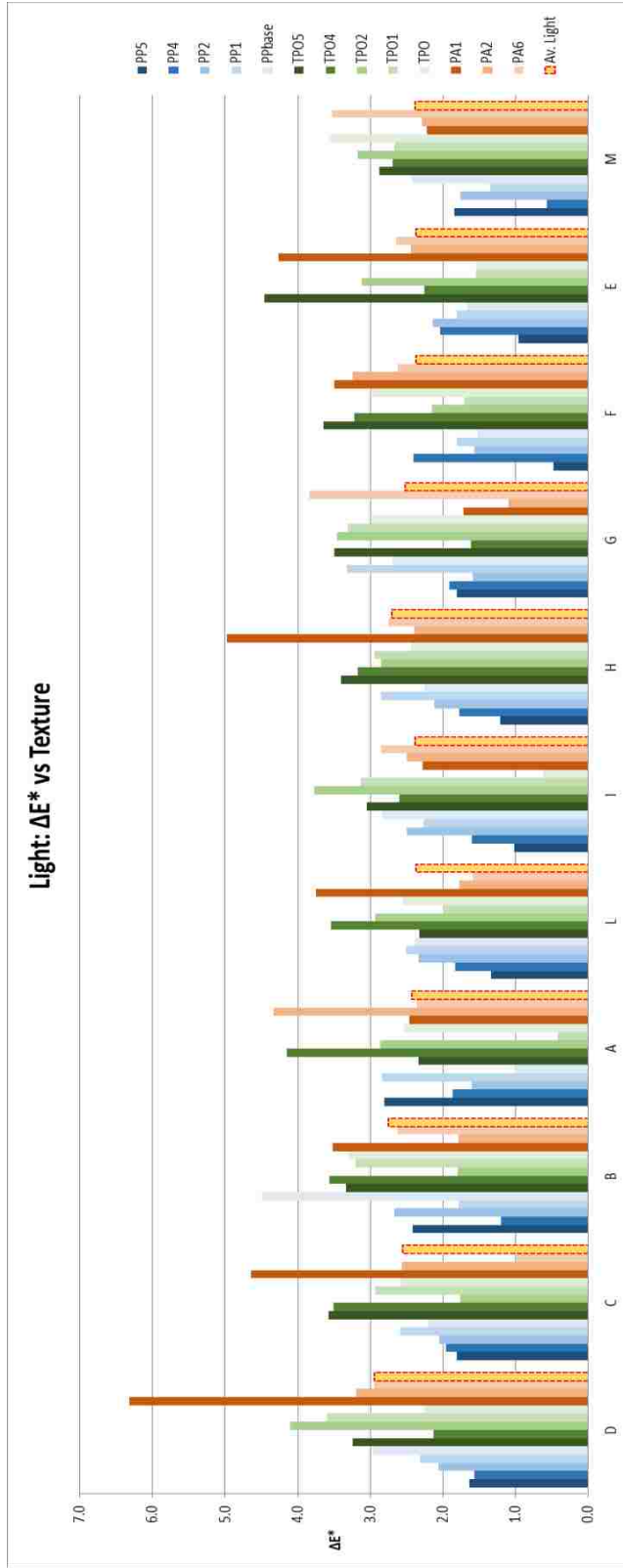


Figure 61. Fingerprint - Light: ΔE^* vs Texture.

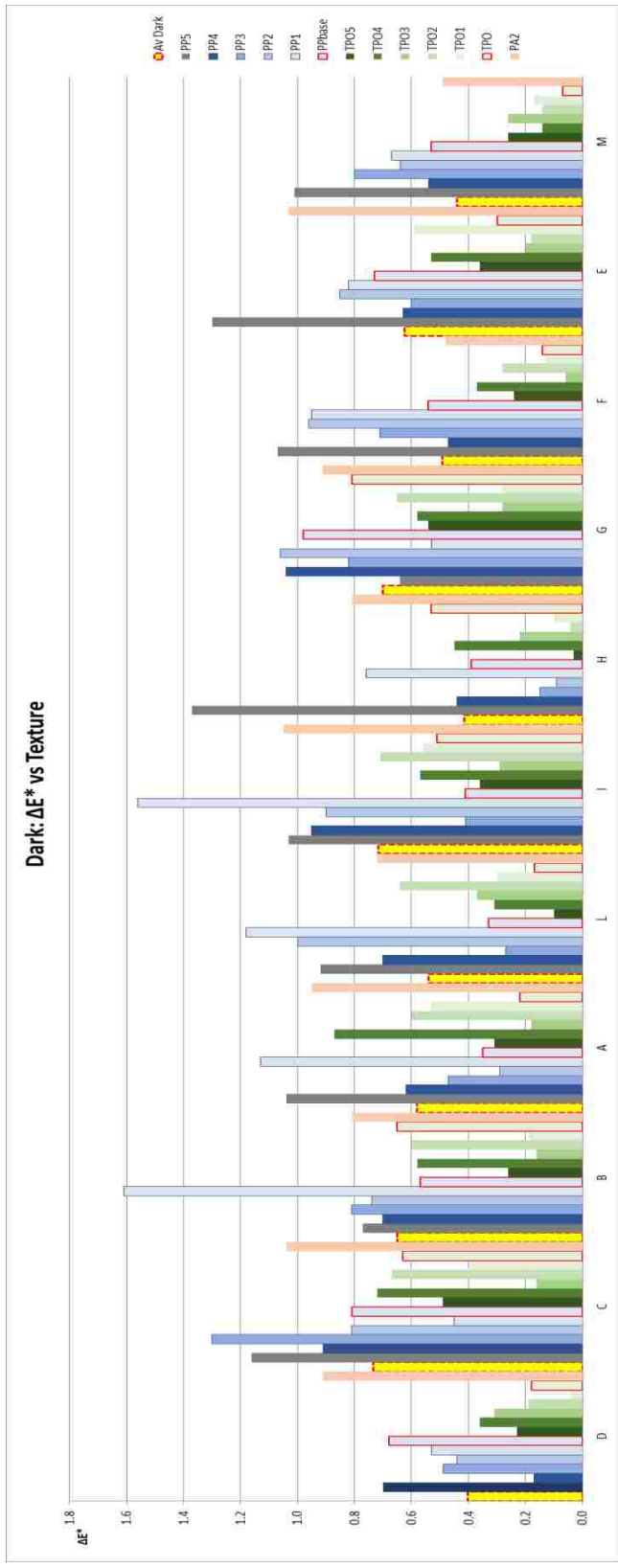


Figure 62. Fingerprint - Dark: ΔE^* vs Texture.

5.6 Fingerprint test – Texture effect

Fingerprint test results organized in order to show the effect of each texture formulation are shown in Figure 63 and Figure 64. As shown in Table 31, *M* performs quite well while *B*, *G* and *C* are among the worst textures. Furthermore, it can be observed that the differences between the $\Delta E_{\text{max-min}}$ of the textures and of the materials, for each color, are the smallest among the test methodologies. Thus in the dusting test the effect of the material is comparable to that of the textures.

Table 31. Fingerprint - Average ΔE^* of each texture.

Texture	Fingerprint test - ΔE^* mean	
	Dark	Light
F	0.68	2.38
M	0.55	2.38
D	0.60	2.95
H	0.64	2.71
L	0.76	2.38
B	0.97	2.75
E	0.73	2.38
C	0.84	2.55
G	0.86	2.53
I	0.86	2.39
A	0.83	2.43
ΔE^* max-min	0.42	0.58

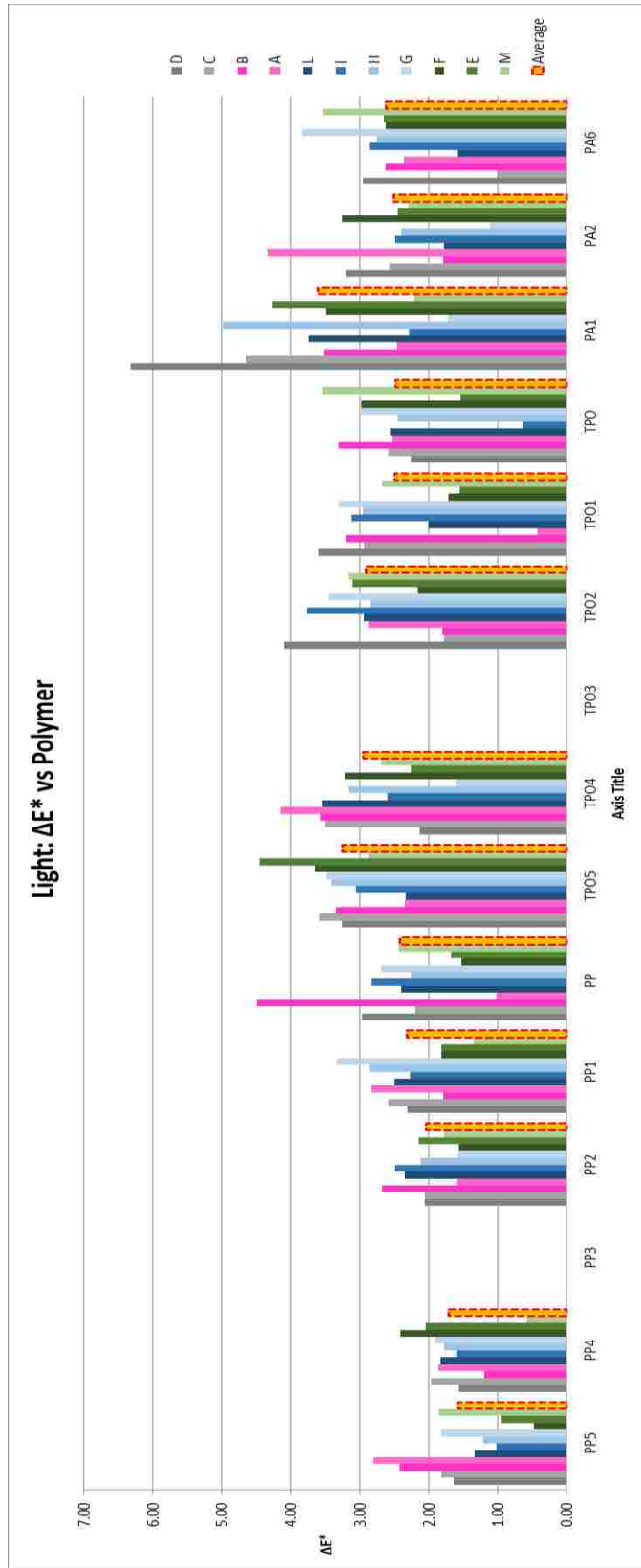


Figure 63. Fingerprint - Light: ΔE^* vs Polymer.

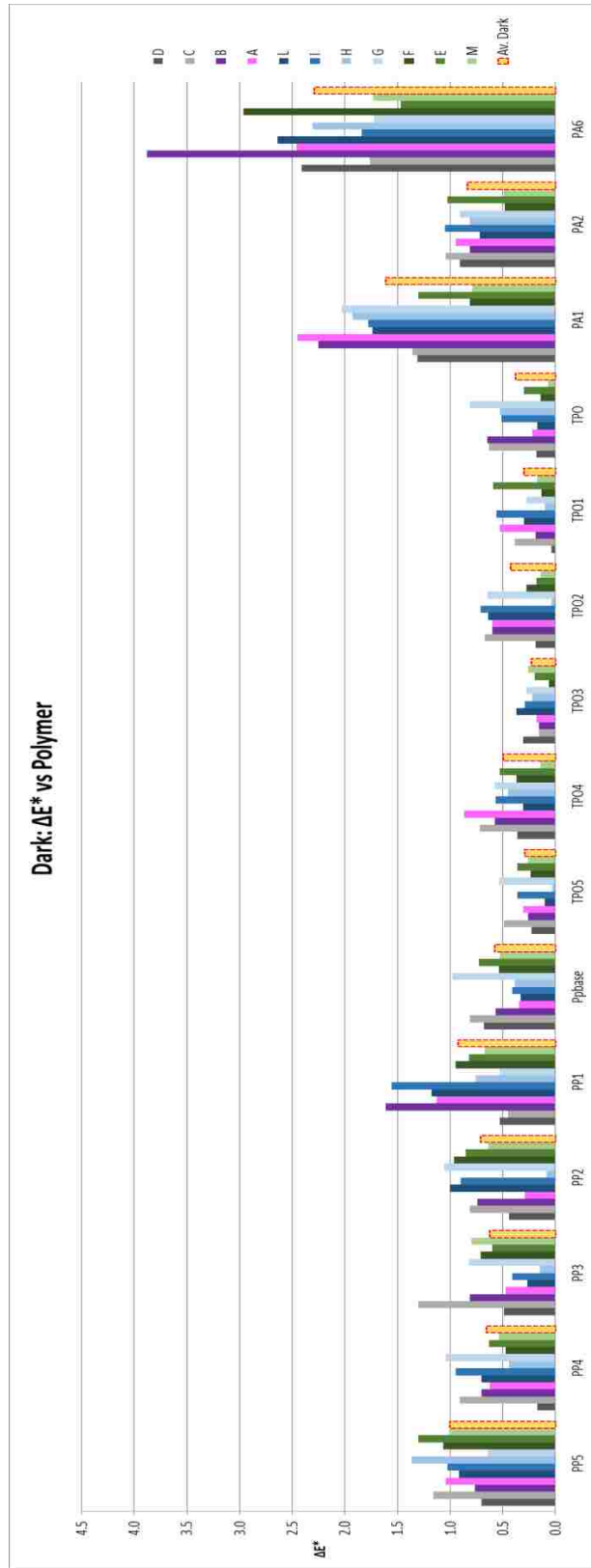


Figure 64. Fingerprint - Dark: ΔE^* vs Polymer.

5.7 Comparison among the outcomes of the test methodologies

In the following the polymer formulations that show the lower ΔE^* are listed according to the polymer category and then according to the test methodology and color. As can be inferred from Table 32 the polypropylene formulation that show the most consistent performances over all the test methodologies and colors are: PP, PP4 and PP5. The thermoplastic polyolefins formulations that show the lowest values of ΔE^* are TPO and TPO1 as can be inferred from Table 33. The polyamide formulation that performs better than the others is PA2 as can be observed in Table 34.

Table 32. Best performing polypropylene formulations for each test.

Best performing polypropylene formulations for each test					
Martindale		Dusting		Fingerprint	
Dark	Light	Dark	Light	Dark	Light
PP, PP2,PP3	PP, PP4	PP, PP1, PP5	PP, PP5	PP, PP3,PP4	PP4,PP5

Table 33. Best performing thermoplastic polyolefins formulations for each test.

Best performing thermoplastic polyolefins formulations for each test					
Martindale		Dusting		Fingerprint	
Dark	Light	Dark	Light	Dark	Light
TPO, TPO1, TPO3	TPO, TPO5	TPO, TPO1, TPO3	TPO1, TPO4	TPO1, TPO3, TPO5	TPO1, TPO4

Table 34. Best performing polyamide formulations for each test.

Best performing polyamide formulations for each test					
Martindale		Dusting		Fingerprint	
Dark	Light	Dark	Light	Dark	Light
PA2	PA1	PA2	PA2	PA2	PA2

The effect of the textures on the results for each test methodology can be assessed in terms of ΔE^* max-min. It is the difference between the highest and the lowest value of ΔE^* of a set of data. The effect of the textures on the results with respect to the effect of the materials can be assessed by comparing the ΔE^* max-min of textures with that of the materials (for a given test methodology and color).

The effect of the textures on the results is lower than the effect of the materials. In particular for the Martindale test the ΔE^* max-min of the textures are much lower than those of the materials, in both colors. These differences are smaller for the Fingerprint test and the smallest for the Dusting test. It is important to observe that the Martindale test which shows the lowest values of range and material variation, has a large difference between material and texture effects in terms of ΔE^* max-min. On the other hand the Fingerprint Dusting test shows large discrepancies and the values of ΔE^* max-min of the textures is comparable to those of the materials. Thus it can be stated that the texture influences the variability of the results of the materials. It can be observed that as the texture effect becomes more important, the variability of the results of the polymer formulations increases.

As can be inferred from Table 35 the textures M, A and B have less propensity to soiling than the others over all the material formulations, colors and test methodologies. The performances of the other textures are not consistent therefore, the worst performing textures were eliminated from further testing. It has been observed that the textures C,

D, G and H are among the worst performing textures in more than one test and never among the best ones.

It is not possible to correlate the microscope observations with the behavior of the textures. For instance the textures C and D have the largest number of cavities while G and H do not. Therefore, the number of cavities cannot be used as a criterion to rank textures as it does not correlate with the data obtained from soiling tests. This also means that the effect of the size of the soiling agent is not influential on the results, while it could be expected that a given texture may be more sensitive to the size of the soiling agents than others.

It is of importance to recall that the test methodologies have different values of applied load and soiling agent. If the effect of the particle size of the soiling agent can be neglected, it is possible to rank the test methodologies according to the increased applied load during testing as follows: Martindale, Fingerprint, Dusting test. Comparing the trend of the applied load in each test with that of the effect of the textures on the propensity to soiling of the materials, it can be observed that an increase in the load causes a decrease in the effect of the textures on the propensity to soiling.

5.8 Test methodologies comparison

In the following the performances of the test methodologies are compared according to two parameters: the range and the material variation. For each test methodology, polymer category (PP, TPO and PA) and color the range is defined as the difference between the maximum and the minimum value of the average color difference of the polymer formulations (i.e. PP1, PP2, PP4 etc). For instance the range identified by the Martindale test on the dark thermoplastic polyolefin samples is computed as the difference between the average values of the TPO2 (max) and of the TPO1 (min). The range is indicated as $\Delta E_{max} - \Delta E_{min}$.

The material variation for each test methodology, polymer category and color is computed as the standard deviation of the average values of each polymer formulation. For instance the material variation of the light polypropylene specimens in the Martindale test is computed as the standard deviation of the average values of color difference of TPO, TPO1, TPO2, TPO4 and TPO5.

The material variation has been computed because the range does not provide any information about the discrepancies of the values in between the maximum and the minimum values. For instance it is possible to find a large range and a little material variation in the case where one value is very different from the others. Nevertheless, the same value of the range with a high material variation corresponds to a more scattered range of data. The test methodologies which show the highest discrepancies are characterized by high values of the range and of the material variability. The comparison is reasonable under the assumption that the effect of the operator on the results of the Dusting test and the Fingerprint test is random therefore, there is not any systematic error that can create a trend.

As can be inferred from Table 35 and Table 36 the Martindale test shows the lowest values of range and material variation, despite the highest value of applied load. It means that the adopted soiling agent influences the results more than the load. In

particular, the Martindale test shows much smaller values of range and material variation for the polyamide formulations in both colors.

Table 35. Test methodology performance parameters: dark formulations.

	Dark Specimens					
	$\Delta E_{max} - \Delta E_{min}$			Material variation		
	Martindale	Dusting	Fingerprint	Martindale	Dusting	Fingerprint
PP	0.37	0.39	0.43	0.14	0.14	0.17
TPO	0.23	0.30	0.27	0.09	0.11	0.10
PA	0.11	0.24	1.45	0.06	0.13	0.73

Table 36. Test methodology performance parameters: light formulations.

	Light Specimens					
	$\Delta E_{max} - \Delta E_{min}$			Material variation		
	Martindale	Dusting	Fingerprint	Martindale	Dusting	Fingerprint
PP	0.26	0.58	0.83	0.11	0.22	0.37
TPO	0.50	1.50	0.77	0.22	0.64	0.33
PA	0.12	1.15	1.09	0.06	0.58	0.60

The Dusting and Fingerprint test on average show the highest discrepancies. The Dusting test produces the highest discrepancies on the dark and light thermoplastic polyolefins and on the dark polyamides, compared to the other tests. Fingerprint test shows large discrepancies for the polypropylenes and polyamides in both colors. The polyamides are used for the door handles that are often in contact with the fingers of the driver and of the passenger. Therefore, the Fingerprint test is suitable for testing the

polyamides. On the other hand the low values of discrepancies observed in the Martindale test are not a main concern because the rubbing action of a cloth on a door handle is less probable to occur than the interaction with the fingers. A complementary aspect to be investigated is the separation of the maximum and minimum values from the value of the baseline material. As can be inferred from

Table 37 – 39 the baseline material is most of the times the one showing the minimum value of color difference in more than one test, as in the case of dark polypropylene.

Table 37. Martindale test - Separation from the baseline

		Martindale test - Separation from the baseline									
		Dark					Light				
		MAX	MIN	Baseline	Sep. Max	Sep. Min	MAX	MIN	Baseline	Sep. Max	Sep. Min
PP	ΔE_{mean} StDev	PP1	PP	Baseline	0.23	0.00	PP1	PP	Baseline	0.26	0.00
		0.59	0.36	0.36			2.23	1.97	1.97		
		0.18	0.24	0.24			0.43	0.17	0.17		
TPO	ΔE_{mean} StDev	TPO2	TPO1	Baseline	0.18	0.05	TPO2	TPO	Baseline	0.37	0.00
		0.45	0.22	0.27			2.02	1.65	1.65		
		0.24	0.22	0.12			0.70	0.19	0.19		
PA	ΔE_{mean} StDev	PA6	PA2	Baseline	0.00	0.11	PA2	PA1	Baseline	0.06	0.06
		1.89	1.78	1.89			2.91	2.78	2.84		
		0.26	0.21	0.26			0.39	0.39	0.23		

Table 38. Dusting test - Separation from the baseline

		Dusting test - Separation from the baseline									
		Dark					Light				
		MAX	MIN	Baseline	Sep. Max	Sep. Min	MAX	MIN	Baseline	Sep. Max	Sep. Min
PP	ΔE_{mean} StDev	PP2	PP	Baseline	0.30	0.00	PP4	PP	Baseline	0.58	0.00
		0.70	0.40	0.40			2.21	1.63	1.63		
		0.27	0.26	0.26			0.72	0.82	0.82		
TPO	ΔE_{mean} StDev	TPO4	TPO	Baseline	0.18	0.00	TPO	TPO4	Baseline	0.00	1.50
		0.55	0.37	0.37			3.30	1.80	3.30		
		0.22	0.28	0.28			1.65	0.47	1.65		
PA	ΔE_{mean} StDev	PA1	PA2	Baseline	0.20	0.04	PA6	PA2	Baseline	0.00	1.15
		0.56	0.32	0.36			2.07	0.92	2.07		
		0.29	0.26	0.14			0.92	0.24	0.92		

Table 39. Fingerprint test - Separation from the baseline

		Fingerprint test - Separation from the baseline									
		Dark					Light				
		MAX	MIN	Baseline	Sep. Max	Sep. Min	MAX	MIN	Baseline	Sep. Max	Sep. Min
PP	ΔEmean StDev	PP5	PP	Baseline	0.43	0.00	PP	PP5	Baseline	0.00	0.83
		1.00	0.57	0.57			2.41	1.58	2.41		
		0.23	0.21	0.21			0.91	0.67	0.91		
TPO	ΔEmean StDev	TPO4	TPO5	Baseline	0.12	0.09	TPO5	TPO	Baseline	0.77	0.00
		0.50	0.29	0.38			3.25	2.49	2.49		
		0.20	0.15	0.25			0.61	0.82	0.82		
PA	ΔEmean StDev	PA6	PA2	Baseline	0.00	1.45	PA1	PA2	Baseline	0.99	0.10
		2.29	0.84	2.29			3.61	2.51	2.61		
		2.50	0.20	2.50			1.39	0.86	0.79		

As can be observed by comparing the data in Table 37 – 39 the Martindale test shows the lowest values of separation of the maximum and of the minimum values with respect to the baseline formulations. However, the values of separations for the light thermoplastic polyolefins are comparable to those of the other tests. Furthermore, the values of separation from the baseline show in more detail that the polyamides are not suitable to be tested adopting the Martindale test methodology as their values are much lower than those recorded with the other tests. The Dusting test shows the highest separation from the baseline and overall the highest separations among all the tests for the thermoplastic polyolefins in both colors and for the light polyamides. As can be inferred from Table 39 the Fingerprint test shows the highest separations for the polypropylenes and polyamides.

These observations are related to the values of range and material variation by definition. Nevertheless, it is of importance to know how the different formulations perform with respect to the baseline material because the aim of the test methodologies is to provide results that allow distinguishing between current production (baseline material) and new materials. On the basis of the results in Table 35 – 39 the Dusting test is particularly suitable for the thermoplastic polyolefins in both colors and Fingerprint test is suggested for testing the polyamides. Furthermore, the Martindale test is not recommended for the polyamides because of the low values of range and separation of the minimum and maximum values from the baseline value.

5.9 Overall soiling test data comparison

5.9.1 Best and worst materials identification from the point of view of soiling prevention

In order to find the best performing formulations the polymers with the top six values of the average ΔE^* have been listed as in Table 40. It can be observed that for dark formulations TPO3, TPO and TPO1 are among the best performing in all the tests and that Martindale and Fingerprint tests results for the dark specimens are quite similar since they feature the same three formulations in their top four values, while very different for the light specimens. Overall it can be inferred that PP, TPO, TPO1 and TPO3 can represent the best polymer formulations for soiling prevention.

Table 40. Best performing formulations for soiling prevention.

Best performing formulations for soiling prevention					
DARK			LIGHT		
Martindale	Dusting	Fingerprint	Martindale	Dusting	Fingerprint
TPO1	TPO3	TPO3	TPO5	PA2	PP5
PP3	PA2	TPO5	TPO	PA1	PP4
TPO3	TPO	TPO1	TPO2	TPO5	PP2
TPO	PP	TPO	TPO4	PP	TPO1
PP	PA6	TPO2	PP	PP5	PP1
TPO4	TPO1	TPO4	PP4	TPO2	PP

Table 41. Worst performing formulations for soiling prevention.

Worst performing formulations for soiling prevention					
DARK			LIGHT		
Martindale	Dusting	Fingerprint	Martindale	Dusting	Fingerprint
PA1	PP4	PA6	PA2	TPO	PA1
PA6	PP2	PA1	PA6	PP4	TPO5
PA2	TPO4	PP5	PA1	PA6	TPO4
TPO5	PA1	PP1	PP5	PP1	TPO2
TPO2	TPO5	PA2	PP1	PP2	PA6
PP4	PP3	TPO4	PP2	TPO4	PA2

In order to find the worst performing formulations for soiling prevention the worse six values of the average ΔE^* for each test have been listed as in Table 41. It can be observed that results are more scattered, nevertheless the following material formulations can be identified as the worst performing: PA1, PA2, PA6, TPO2, TPO4, TPO5, PP1, PP2, PP3, PP4, PP5. As can be seen in Table 40, PA2 performs quite well on both colors in the Dusting test while according to the results shown in Table 41 it is ranked among the worst in the Martindale and Fingerprint tests.

5.9.2 Best and worst textures identification from the point of view of soiling prevention

In order to find the textures with the best soiling prevention capabilities, the top four values of the average ΔE^* have been listed as in Table 42. In this case four values only have been considered since the textures are less than the polymer formulations and since the aim of the experimental work is that of skimming the lowest values in order to proceed with further moldings of the remaining textures and polymer formulations. It can be observed that A and B perform well in the Martindale and Dusting tests while the texture showing the most consistent performance is M.

Table 42. Textures with the best soiling prevention capabilities

Textures with the best soiling prevention capabilities					
DARK			LIGHT		
Martindale	Dusting	Fingerprint	Martindale	Dusting	Fingerprint
<i>A</i>	<i>I</i>	<i>H</i>	<i>B</i>	<i>B</i>	<i>A</i>
<i>B</i>	<i>B</i>	<i>D</i>	<i>A</i>	<i>L</i>	<i>F</i>
<i>E</i>	<i>A</i>	<i>M</i>	<i>C</i>	<i>M</i>	<i>I</i>
<i>M</i>	<i>E</i>	<i>L</i>	<i>M</i>	<i>A</i>	<i>M</i>

In order to find the worst performing textures from the point of view of soiling prevention, the worse six values of the average ΔE^* for each test have been listed as in Table 35. It can be observed that the worst performing textures are: C, D, G and H. It must be mentioned that there are other textures that show poor performances in some tests yet some of them are also ranked among the best performing for some other tests. A good example is B that is performing quite bad in the Fingerprint test but it was one of the top values in Martindale and Dusting.

Table 43. Worst performing textures.

Worst performing textures					
DARK			LIGHT		
Martindale	Dusting	Fingerprint	Martindale	Dusting	Fingerprint
<i>I</i>	<i>H</i>	<i>G</i>	<i>I</i>	<i>E</i>	<i>D</i>
<i>D</i>	<i>F</i>	<i>I</i>	<i>E</i>	<i>F</i>	<i>B</i>
<i>G</i>	<i>L</i>	<i>C</i>	<i>D</i>	<i>H</i>	<i>H</i>
<i>L</i>	<i>D</i>	<i>B</i>	<i>H</i>	<i>C</i>	<i>C</i>
<i>H</i>	<i>G</i>	<i>F</i>	<i>G</i>	<i>D</i>	<i>G</i>
<i>C</i>		<i>A</i>	<i>F</i>	<i>I</i>	<i>L</i>

5.10 Surface hardness measurements

Vickers hardness measurement of the specimens has been performed as the last step of the experimental work. As mentioned in chapter 4 the same texture, the smoothest, has been chosen for all the polymer formulations. Nevertheless, it was not smooth enough in order to obtain measurements that could allow us to identify any difference within each class of polymers as can be seen in Table 38, Table 39, and Table 40. As a general indication PA formulations have a higher surface hardness than PP ones which in turn show higher values with respect to TPO formulations.

Table 44. Vickers hardness of the PA formulations.

	PA6	PA1	PA2
	[HV]	[HV]	[HV]
Average	22.7	14.3	21.8
StDev	3.4	1.5	6.5

Table 45. Vickers hardness of the TPO formulations.

	TPO	TPO1	TPO2	TPO3	TPO4	TPO5
	[HV]	[HV]	[HV]	[HV]	[HV]	[HV]
Average	4.0	6.7	4.2	4.3	3.7	4.3
StDev	0.1	0.2	0.4	0.4	0.1	0.3

Table 46. Vickers hardness of the PP formulations.

	PP	PP1	PP2	PP3	PP4	PP5
	[HV]	[HV]	[HV]	[HV]	[HV]	[HV]
Average	6.1	6.1	8.6	6.8	6.6	8.8
StDev	0.6	0.3	0.5	0.5	0.1	0.4

5.11 Surface energy evaluation

Surface energy has been evaluated starting from the water contact angle between a water droplet and the surface of the specimen. Water contact angle values are affected by very high errors because of the limitations of the available means and the intrinsic difficulty in performing such measurements. As shown in Table 47 the obtained values do not allow us to distinguish among the different formulations within each category of polymers. As a general indication PA formulations have a higher surface energy than TPO ones which on turn show higher values with respect to PP formulations. The poor performances of the PA formulations can be due to their high surface energy because as mentioned in Chapter 3 a higher the surface energy, greater is the tendency of creating bonds.

Table 47. Water contact angle of each polymer formulation.

					Average	StDev
Light specimens	PA	PA6	WCA	[deg]	75	4
		PA1	WCA	[deg]	73	4
		PA2	WCA	[deg]	74	3
	PP	PP	WCA	[deg]	95	5
		PP1	WCA	[deg]	93	3
		PP2	WCA	[deg]	98	5
		PP4	WCA	[deg]	99	6
		PP5	WCA	[deg]	101	5
	TPO	TPO	WCA	[deg]	84	4
		TPO1	WCA	[deg]	85	4
		TPO2	WCA	[deg]	83	4
		TPO4	WCA	[deg]	84	4
		TPO5	WCA	[deg]	87	4

5.12 Effect of the influencing factors

Water contact angle and surface hardness measurements do not allow us to distinguish among the formulations within each polymer category because the errors affecting the measurements are high. This is mainly due to the fact that the surfaces were not flat and were textured. Nevertheless, the available values of water contact angle and surface hardness can be correlated to the performances of the polymer categories (PP, TPO and PA).

According to the estimated surface energy it is possible to state that the polypropylenes have the lowest surface energy, the thermoplastic polyolefins an intermediate value and the polyamides the highest one. Therefore, conforming to the adhesion theory mentioned in the literature review the polyamides are expected to have a higher propensity to soiling than the thermoplastic polyolefins which in turn would have a larger propensity to soiling than the polypropylenes.

A material is assumed to perform better than another in a test, from the point of view of soiling prevention, if in the top six values of Table 40, for each color it is possible to see more formulations of that material than of any other. The result is to be compared with the outcome of the worst performing formulations, identified using the same criterion but applied to the data in Table 41. For instance in the Martindale test the light thermoplastic polyolefins perform better than the other polymers, because four values out of six in the Ligh- Martindale column of the Table 40 are TPO formulations and at the same time there are not any TPO formulations in the same column of the Table 41.

Analyzing the results of chapter 5.9.1 with this criterion, it can be observed that both color formulations of the thermoplastic polyolefins perform better than the polypropylenes in the Martindale test. Furthermore, in the Fingerprint test the best performing light material is the thermoplastic polyolefin while the best performing dark material is the polypropylene. In addition in the Dusting test the polyamide show good soiling resistance when compared to the other materials, while the performances of the thermoplastic polyolefins and of the polypropylenes are similar. Considering that these

results do not match with the ones expected, it is possible to conclude that the surface energy is not an influencing factor.

The hardness measurements show that the polyamides are the hardest polymers, followed by the polypropylenes and the thermoplastic polyolefins (softest). It can be observed that in both tests where a load is applied, Fingerprint and Martindale tests, the polyamide show a high propensity to soiling. On the other hand when there is not any applied load the polyamides show a soiling resistance comparable to that of the thermoplastic polyolefins and of the polypropylenes. It can be stated that when a load is applied from a value of hardness higher than 20 ± 4 HV (average hardness of the polyamides) on, the propensity to soiling of a polymer increases with the hardness. The fluctuations in the performances of the polypropylenes and of the thermoplastic polyolefins mentioned above show that when the hardness values are lower than 7 ± 2 HV (average hardness of the polypropylenes) they cannot be related to the propensity to soiling of the polymers.

The flexural modulus values in Table 5 and the observations made for the surface energy and surface hardness lead to the conclusion that when soiling occurs with the application of a load, a polymer with a high value of flexural modulus is more prone to soil than one with a lower value of flexural modulus. Nevertheless, this trend does not occur for values of flexural modulus as low as those of the polypropylene and of the thermoplastic polyolefins as can be inferred by the fluctuation in their performances.

6. Conclusion

Test methodologies

A test methodology is more suitable for testing a category of polymers (PP, TPO, PA) if it shows the highest values of discrepancy and separation from the baseline formulations of the minimum and maximum values. According to these criteria the Dusting test is suitable for testing the thermoplastic polyolefins and the Fingerprint test is suggested for testing the polyamides and polypropylenes. Furthermore, It is of importance to mention that the polyamides are adopted for the door handles which interact with the fingers of the passengers and of the driver, therefore the Fingerprint test is preferable for testing the polyamides also for its similarity with the real soiling scenario. The Martindale test shows the lowest values of the performance indicators mentioned at the beginning. The values polyamides in particular are the lowest. Thus the Martindale test does not allow identifying the differences among the polyamides.

Polymer formulation

In order to identify which are the best performing polymer formulations from the point of view of soiling prevention the results in Table 32 - 34 have been considered. In particular a formulation is considered the best performing if it is the most recurrent when considering the outcomes of all the test methodologies. According to this criterion the best performing polyamide formulation is PA2 because with reference to Table 34, it is the most recurrent formulation. The best performing thermoplastic polyolefin formulations are TPO and TPO1 while the best performing polypropylene formulations are PP and PP4. The formulations TPO3 and PP3 have not been considered since they come just in the dark color. It can be observed that the baseline material is performing better than the other formulations in the case of the polypropylene and of the

thermoplastic polyolefin while it is almost always among the worst in the case of the polyamides.

Texture

It has been observed that the textures influence the propensity to soiling of the specimens of the same materials. Furthermore, the effect of the textures on the propensity to soiling of the specimens is lower than the effect of the materials and decreases with the applied load during soiling. It has also been observed that when the effect of the texture grows with respect to that of the materials, the discrepancies among the results of each test methodology increase. Therefore, it is possible to expect that the plastic components in the passenger compartment which are subject to soiling with an applied load will show less variation in soiling propensity when changing texture.

The textures that have less propensity to soiling than the others over all the material formulations, colors and test methodologies are A, B and M. The performances of the other textures are not consistent nevertheless; it has been observed that the textures C, D, G and H are among the worst performing textures in more than one test.

The analysis of the microscope magnifications of the worst and of the best performing textures, showed that the relative dimensions of the cavities with respect to the size of the particles of the soiling agents do not influence the propensity to soiling of the specimens.

Effect of the influencing factors

Water contact angle and surface hardness measurements are not suggested for the analysis of the textured specimens obtained by cutting the gloveboxes because the

errors affecting the measurements are too large to allow the comparison among the formulations of each polymer category.

According to the estimated surface energy it is possible to see that the polypropylenes have the lowest surface energy, the thermoplastic polyolefins an intermediate value and the polyamides the highest one. Thus conforming to the adhesion theory the polyamides are expected to have a higher propensity to soiling than the thermoplastic polyolefins which in turn would have a higher propensity to soiling than the polypropylenes. Considering that the measured values do not match with the ones expected, it is possible to conclude that the surface energy is not an influencing factor.

The hardness measurements show that the polyamides are the hardest polymers, followed by the polypropylenes and the thermoplastic polyolefins (softest). Analyzing the results, a correlation between hardness, propensity to soiling and applied load during testing can be observed. In particular a large value of hardness and applied load correspond to a high propensity to soiling. Furthermore, hardness values lower than 7 ± 2 HV (average hardness of the polypropylenes) cannot be related to the propensity to soiling of the polymers independently of the applied load. Therefore, the measurement of surface hardness is not suitable for analyzing the soiling prevention capabilities of the polymers under examination.

The flexural modulus values lead to the conclusion that when soiling occurs with the application of a load, a polymer with a high value of flexural modulus is more prone to soil than one with a lower value of flexural modulus. Nevertheless, this conclusion does not hold for values of flexural modulus as low as those of the thermoplastic polyolefins independently of the applied load. Therefore, the flexural modulus is not of suggested for the evaluation of the propensity to soiling of the thermoplastic polyolefins and of the polypropylenes.

7. Recommendations

For future studies on this topic, some changes and improvements can be performed:

- Replication of the tests using samples from different production batches would improve the reliability of the results and help assess the reproducibility of the test methodologies.
- The effectiveness of the test methodologies in terms of discrepancies could be then assessed because it would be possible to see the effect of the human operator in the Dusting and Fingerprint tests.
- It would be of interest to measure the surface resistivity of the specimens because electrostatic interactions are significant for polymeric materials [24].
- The adoption of a light soiling agent for the Martindale test is also suggested in order to better highlight the performances of the dark specimens.
- The consistency of fingerprint tests could be improved by identifying the load to be applied and designing a machine that could perform this task instead of the human operator.

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