

New eco-coatings based on natural dyes and aqueous polyurethane dispersions

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Abstract

At present, there are an increasing interest at industrial level by the N-methyl pyrrolidone (NMP) free polyurethane aqueous dispersion, due to the limitations posed to this solvent in the latest years in Europe. Among the several applications of coatings, the protection and decoration of objects is one of the most used. Decoration requires color control and new ways to generate long-lasting colors. However, these products are traditionally based on synthetic dyes, which have a lack of compatibility with the aqueous medium resulting in phase separation or agglomerations phenomena. Herein, the use of hydrophilic natural dyes can be envisaged as a viable alternative, once these dyes nature increases their compatibility with the aqueous medium, leading to the increasing of the final product stability along the time. In this context, the present work was devoted to the development of new eco-coatings based on natural dyes and in polyurethanes aqueous dispersions exempt of NMP.

For this study, a polyurethane aqueous dispersion based on isophorone diisocyanate and propylene glycol polyol was synthesized. After, the dispersion properties like solids content, viscosity, pH and particle size were evaluated. Then, coatings added with carminic acid and spirulina blue dyes were produced by solvent casting, by incorporating dyes contents of 0.2, 0.5, 1.0, 1.5 and 2.0% (w/w) into the dispersion. The films obtained after drying were characterized in terms of chemical structure by Fourier Transform Infrared Spectroscopy, which showed the lack of influence of the dyes chemical structure on the polyurethane films, even for the higher content tested. Differential Scanning Calorimetry evidenced the effect of the dye on the films thermal behavior, once when 2% of dyes were added, the values of melting temperature (T_m) and the melting enthalpy variation (ΔH_m) increased for values higher than the base film. Thermogravimetric Analysis showed an increase of the film's thermal stability as the dyes content was increased. The colorimetric analysis was made in order to inspect the color variation due to the dye type and content used. By comparing the base film color with the dyed films, an increasing on the color variation was detected for both dyes. However, for the films containing Spirulina blue this increased with the dye content rising, reaching a maximum value of 65.58 for 2%Sp. In opposition, for carminic acid, the color variation reached a maximum value of 70.62 for 1.0%Cr, being constant for the higher dye contents. In a general way this study evidences the positive effect of the utilization of natural dyes together with friendly polyurethane aqueous dispersions for the production of innovative coatings.

Resumo

Atualmente, a nível industrial regista-se um interesse crescente na utilização de dispersões aquosas de poliuretano isentas de N-metil pirrolidona (NMP), devido às limitações impostas a este solvente na Europa, nos últimos anos. Entre as diversas aplicações dos revestimentos, a proteção e decoração de objetos é uma das mais utilizadas. A decoração requer o controlo das cores e novas formas de gerar cores duradouras. No entanto, estes produtos são tradicionalmente baseados em corantes sintéticos, os quais apresentam falta de compatibilidade com o meio aquoso, resultando em fenómenos de separação de fases ou de aglomeração. Neste contexto, o uso de corantes naturais hidrofílicos pode ser considerado como uma alternativa viável, uma vez que a natureza destes aumenta a sua compatibilidade com o meio aquoso, incrementando a estabilidade do produto final ao longo do tempo. Neste contexto, o presente trabalho foi dedicado ao desenvolvimento de novos eco-revestimentos baseados em corantes naturais e em dispersões aquosas de poliuretanos isentas de NMP.

Neste estudo, procedeu-se à síntese de uma dispersão aquosa de poliuretano baseada em diisocianato de isoforona e propilenoglicol. Seguidamente avaliaram-se as seguintes propriedades da dispersão: teor de sólidos, viscosidade, pH e tamanho de partícula. Na etapa seguinte produziram-se filmes base (sem corantes) e modificados através a adição dos corantes ácido carmínico e azul da spirulina, pelo método de *solvente casting*, incorporando os seguintes teores 0,2, 0,5, 1,0, 1,5 e 2,0 % (m/m). Os filmes obtidos após a secagem foram caracterizados em termos de estrutura química por Espectroscopia de Infravermelho com Transformada de Fourier, que mostrou a ausência de contribuições da estrutura química dos corantes nos filmes do poliuretano, mesmo para o maior teor testado. Através da *Differential Scanning Calorimetry* verificou-se que o efeito do corante no comportamento térmico dos filmes resultou no incremento de temperatura de fusão (T_m) e entalpia de fusão (ΔH_m), dado que quando se incorporou 2% dos corantes estes aumentaram para valores superiores aos obtidos para o filme base. A análise termogravimétrica mostrou um aumento da estabilidade térmica dos filmes com o incremento do teor de corantes. Através da análise colorimétrica avaliou-se a variação de cor devido ao tipo de corante e ao teor utilizado. Ao comparar a cor dos filme de base com a dos filmes modificados com o corante, verificou-se um aumento da variação de cor, para os dois corantes testados. No entanto, para os filmes contendo azul da spirulina, esta variação aumentou com o incremento do teor do corante, atingindo um valor máximo de 65,58 para a amostra 2%

Sp. Em oposição, para o ácido carmínico, a variação de cor atinge um valor máximo de 70,62 para 1,0% de Cr, sendo constante para os teores mais elevados.

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List of Abbreviations

Cr Carminic acid dye

DBA N-dibutylamine

DMPA Dimethylol propionic acid

DMF Dimethylformamide

DSC Differential Scanning Calorimetry

FTIR Fourier Transform Infrared Spectroscopy

IPDI Isophorone diisocyanate

NCO Isocyanate group

PUB Base coating

0.2%Cr Coating modified with 0.2% of Carminic acid dye

0.5%Cr Coating modified with 0.5% of Carminic acid dye

1%Cr Coating modified with 1% of Carminic acid dye

1.5%Cr coating modified with 1.5 % of Carminic acid dye

2%Cr Coating modified with 2% of Carminic acid dye

0.2%Sp Coating modified with 0.2% of Spirulina dye

0.5%Sp Coating modified with 0.5% of Spirulina dye

1%Sp Coating modified with 1% of Spirulina dye

1.5%Sp coating modified with 1.5 % of Spirulina dye

2%Sp Coating modified with 2% of Spirulina dye

PUD Polyurethane-urea aqueous dispersions

PU Polyurethane

Sp Spirulina dye

TG Thermogravimetric analysis

T_g Glass transition temperature

T_m Melting temperature

THF Tetrahydrofuran

VOC Volatile organic compound

ΔH_m Melting enthalpy variation

w/w Mass ratio

INTRODUCTION

1 *Motivation and objectives*

Coatings are polymeric materials used as protective and embellishment agents of several substrates that are expected to maintain its properties along many years under aggressive environments. However, the coatings industry is known by the environmental damage provoked during the products manufacture and application. In order to overcome these drawbacks, the efforts made by the regulatory agencies together with the researcher's, improved the environmental footprint of the coatings industry over the last several decades. Significant reductions in hazardous air pollutants, releases of volatile organic compounds (VOCs) and hazardous waste have been reached, mainly due the turnover for the usage of water based polymeric materials.

In fact, the use of environmentally friendly coatings technologies such as waterborne, powder and high solids materials have been increasing. Herein, coatings based on polyurethane aqueous dispersions were one of the greener alternatives found. Presently, there are an increasing interest at industrial level by the N-methyl pyrrolidone (NMP) free dispersions, due to the limitations posed to this solvent in the latest years in Europe.

Additionally, one of the traditional application of coatings involve the protection and decoration of objects. Decoration requires color control and new ways to generate long-lasting colors. However, these decorative coatings are conventionally based on synthetic dyes, which incorporated into the coatings by mixing, as a post-formulation. One of the major issues related with this strategy is the lack of compatibility of the dyes with the aqueous medium that result in phase separation or agglomerations phenomena. Herein, the use of hydrophilic natural dyes can be envisaged as an interesting alternative, once these dyes nature increases their compatibility with the aqueous medium, leading to increasing of the final product stability along the time. Moreover, natural dyes are known by possessing interesting properties such as antimicrobial or antioxidant activities, which can impart novel properties to the coatings, namely increase the lifetime due to the reduction of the oxidative phenomena that affect the polymer or to confer antimicrobial properties to the coating, beyond the coloring effect. In this context, the present work will be devoted to the development of new eco-coatings based on natural dyes and in polyurethanes aqueous dispersions exempt of NMP.

The work will be organized in the following stages:

- Selection of the natural dye and synthesis of the polyurethane aqueous dispersions using the modified pre-polymer process in order to obtain an NMP-free product;
- Characterization of the polyurethane dispersions in terms of the properties more interesting for the final application, namely by evaluating the solids content, pH and viscosity;
- Preparation of the dyed coating by mixing the selected dye with the final dispersion (post-formulation), testing different dye concentrations.
- Characterization of the coating dyed films in terms of chemical structure, thermal behavior and stability. Moreover, the color of the final coating's films will be also evaluated.

In order to achieve these objectives, the following sections will be devoted to the bibliographic revision of the main coatings used, with a particular focus on the water-based polyurethane coatings, synthesis process and main properties, as well as the conventional strategies used for dyes incorporation into the coatings and the methodologies used for the coatings characterization.

2 *Literature review*

2.1 *Water-based coatings*

Coatings are used in different areas of everyday life. They are used mainly for two purposes: (1) the protection of materials from chemical and physical external attacks, and (2) decoration of objects in order to impart an attractive appearance. The protective function includes resistance against weather damage, decay and corrosion, combined with improved superficial mechanical properties, such as greater impact and abrasion resistance. The decorative effect may be obtained through color, gloss or texture or a combination of these properties.

Table 1 presents a summary of the different types of waterborne coatings. The advantages of these products use are related with good properties under the final application conditions and with their environmentally friendly chemical character. The following advantages can be mentioned:

- ◆ Good resistance to heat and abrasion;
- ◆ Provide excellent adhesion;
- ◆ Low toxicity and flammability due to low VOC emissions;
- ◆ Comparatively to solventborne counterparts, less coating is required to cover the same surface area;
- ◆ The accessories used for the coating application can be cleaned easily with water or water-based solutions and do not require organic solvents;
- ◆ Can be applied by conventional application techniques such as brush or spray.

Table 1 Types of waterborne coatings

Types of water-based coating	Applications	Properties
Waterborne Epoxy	Food and beverage facilities areas (Hart S et al, 1996).	Durable finishing; Corrosion, impact and abrasion resistant; Low odor
Metal Acrylic	Construction in general; Interior or exterior areas where color and gloss retention are important.	Resistant to corrosion, chemicals, u/v light, fumes, some acids and alkalis; Excellent adhesion to substrate without primer.
Waterborne Acrylic	High light reflectance areas Structural steel; Wood	High flashpoint; Low odor. (Fleischmann et al, 2015).
Water Reducible Emulsion	Interior wall paint; Woodwork;	Available in white only; VOCs exempt; Easy to clean; Low odor.
Water Reducible Alkyds	Steel, aluminum, and plastics; General purpose primers and topcoats.	Similar gloss, flow, and leveling properties to the solvent-based alkyd; Easy cleanup.
Acrylic-Epoxy Hybrids	General metal finishing with good hardness, flexibility, and corrosion resistance.	Short pot life; Formulation based on of two or three components.
Polyurethane Dispersions	Primarily wood finishing; metals, textiles, leather, glass, and rigid plastics.	Low VOCs;

2.2 Coating based on water-based polyurethanes

Among the several waterborne products, the water-based polyurethane coatings are having a great attention in the latest years. The main motivation for this growth is related with these products low toxicity and environmentally friendly character once they have only residual amounts or are completely exempt of solvents and volatile organic compounds (VOCs). In addition, these products have a comparable or even superior performance towards the solvent-based counterparts (Hart et al,1996).

Polyurethane dispersions (PUDs) or water-based polyurethanes (WBPU) are an important and versatile group of products that can be used as inks, or protective or decorative coatings. Technical quality has improved dramatically during the past decade due to the development of the dispersion technology, formulations, and application techniques. Plus, current or pending legislation is imposing the reduction of the VOC release (Falco, 2007).

Regarding the application field, due to the versatile properties, WBPU are used from highly flexible to tough coatings for textiles and leather or hard coatings for the protection of wood, metal, concrete, and plastic surfaces, among others (Hart et al, 1996). The coatings properties imparted are related with glossiness, transparency, flexibility impact resistance, abrasion resistance, non-flammability, and adhesion to most substrates. Important applications include wood lacquers, plastic coating and paints (Fleischmann et al, 2015).

Considering the synthesis of the WBPU, chemically speaking, the polyurethanes are polymers containing the urethane (or carbamate) group, which is generated through the reaction of the isocyanate group (NCO) with the hydroxyl group (OH). This reaction can be based on compounds containing two or more isocyanate groups with another bi- or polyfunctional alcohol, usually named polyol. The diversity of the polyurethane properties is related with the wide range of raw-materials that can be used for its synthesis (Falco, 2007). Beyond the OH group, the NCO group presents also reactivity with amines forming ureas, with water that generates an amine and CO₂, and also with organic acids generating amines and CO₂. Nevertheless, the NCO can also react with urethane group forming allophanates and with urea groups resulting in biurets. However, these reactions correspond to the formation of chemical crosslinking, which must be avoided when linear polyurethanes are required (Fernandes, 2017).

The WBPU are a type of polyurethanes that have the particularity of being water-compatible, in opposition with the other classes of this polymer. This is achieved through the incorporation of hydrophilic ionic moieties into the polyurethane molecular structure, rendering a molecular structure where hydrophilic points are distributed into hydrophobic chains. WBPU are defined as binary colloidal systems in which the PU particles are dispersed in a continuous aqueous phase (Kim, 1996). These polymers present a particular property: the viscosity is independent on the polymer molecular weight, being related with the dispersion particle size. WBPU present a film forming mechanism dependent of the water evaporation and polymer crystallization (Santos, 2018). WBPU can be produced by using long-chain polyether, polyester or polycarbonate polyols, diisocyanates (usually aliphatic ones in order to reduce the reactivity towards the water

during the dispersion stage), low molecular weight glycols and/or diamines, bis-hydroxycarboxylic acids (internal emulsifier) and a neutralizing base (Kim, 1996).

In what concerns the main processes used for WBPU synthesis, the acetone and the prepolymer processes are typically employed. Both processes have the following stages:

- ◆ Synthesis of an NCO-terminated prepolymer in bulk;
- ◆ Prepolymer dispersion in water;
- ◆ Chain extension.

In the acetone process, a prepolymer ended in NCO groups is prepared using acetone as solvent. Then, the next stage corresponds to the chain extension, where a sulphonated diamine is used as chain extender and also internal emulsifier. After, in the next stage, the dispersion in water is formed by adding this solvent to the polymer solution under stirring. The last stage corresponds to the acetone removal by distillation in order to obtain the WBPU (Pérez-Limiñana et al., 2006).

In the case of the prepolymer process, the polyurethane terminated prepolymer is synthesized in the first stage, where the hydrophilic groups are introduced on the polymer molecular structure. Here, the polyol, the dimethylol propionic acid (DMPA) based as internal emulsifier (dissolved in N-methyl-2-pyrrolidone (NMP)), the diisocyanate and the catalyst are putted into the reaction vessel. The solvent NMP is required for the DMPA dissolution, due to its low solubility in the reactive medium. The reaction temperature is usually set at 80°C. After, the next stage corresponds to the ionic group's neutralization at a temperature between 30-60°C, by adding a tertiary diamine. This reaction ionizes the acid groups of DMPA forming ionic sites. Then, the prepolymer dispersion in water is formed by adding this solvent under vigorous stirring. Afterwards, the chain extension is made by adding a diamine in order to react with the residual NCO groups available on the prepolymer (Santos, 2018). Regarding the use of NMP, this solvent has a boiling point around 200°C and will remain in the final dispersion. However, the use of this solvent was limited by the European Commission due to its recent classification as carcinogenic, mutagenic and toxic for reproduction. Here, products with more than 5% of NMP are classified as toxic, and those containing less than 5% are labeled as irritant, since 2015. This imposition resulted on the development of new process for WBPU synthesis. In this sense, a new process was developed, by modifying the traditional prepolymer process. Here, the modification of the prepolymer synthesis stage was done, allowing the addition of the pre-neutralized DMPA in acetone (DMPA was previously dissolved in acetone in the presence of the neutralizing agent, triethylamine). Then, due to the low boiling point of acetone, the prepolymer synthesis stage was

divided in two steps: (1) Reaction of the polyol with the isocyanate at 80°C; (2) Reaction of the pre-neutralized DMPA with the residual isocyanate from step (1) at 55°C. The following stages of the process correspond to the prepolymer dispersion in water and the chain extension. A last stage of acetone removal was introduced (Fernandes, 2017). This process is drawn in Figure 1.

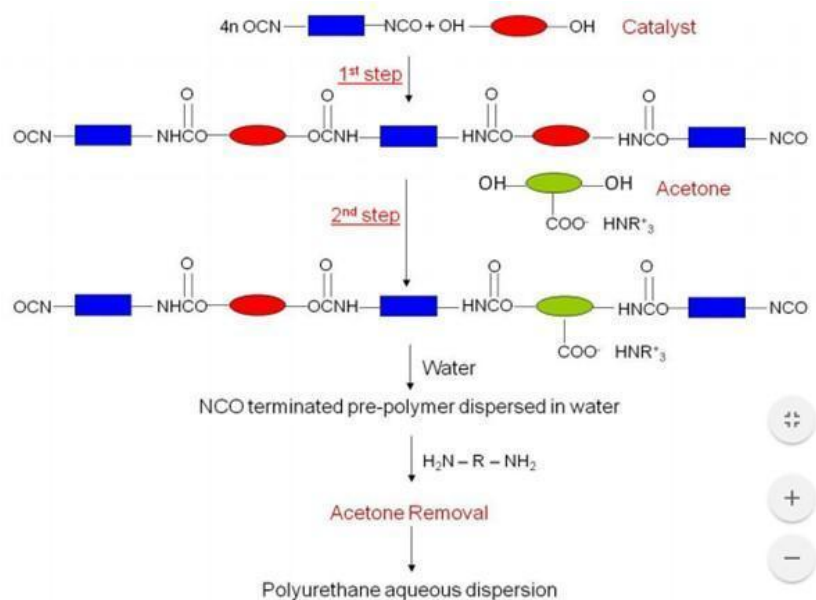


Figure 1 Schematic representation of the modified pre-polymer process (Adapted from Fernandes, 2017).

3 Strategies used for dyes incorporation into the coatings

The formulation of dyed polymers is a research field of great potential with regard to high-performance materials. Colored polymers have become increasingly important as materials for a miscellaneous of technical applications in recent years.

Dyes are coloring agents widely used in the textile, pharmaceutical, food, cosmetics, plastics, among others. The colored coatings are mainly produced by two approaches: through the dye post-mixing into the polymer before the application or by imbedding the dye into the polymer molecular structure, by chemical reaction, during the polymer synthesis.

The first approach is widely used once it allows the usage of a variety of colors, by preparing the coating: dye mixture according to the intended color. This process have advantages once the dye can it be easily added, and it is simple and low cost to implement. However, the main drawbacks associated to this process are related with the lack of chemical bond between the dye and the

polymer, once it is only attached by means of physical interactions and the absence of chemical compatibility between the dye and the coating solution, can limit the pot life of the mixture (Van Der Schueren L et al, 2013). Despite this, no publications were found about the use of this procedure with natural dyes. Their hydrophilic nature can result on an increasing of the water-based coating:dye compatibility, rendering better dispersion into the coating film.

Regarding the imbedding the dye into the polymer molecular structure, by chemical reaction the dye-containing polymers are an important class of coatings with a comprehensive scope and a focus on azo, triphenylmethane, indigoid, perylene and anthraquinone dyes, which chemical structure is shown in Figure 2.

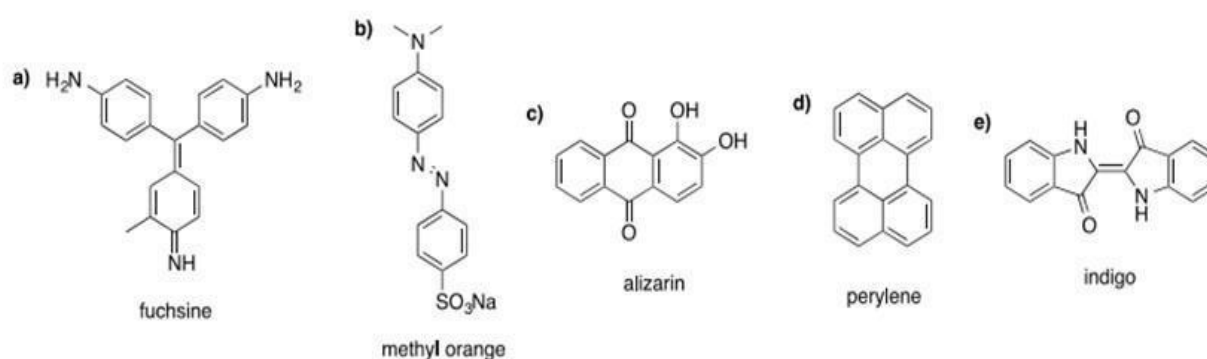


Figure 2 Characteristic representatives of (a) triphenylmethane dyes, (b) azo dyes, (c) anthraquinone dyes, (d) perylene dyes, and (e) indigoid dyes (Adapted from Fleischmann et al, 2015).

There are several approaches towards the preparation of such materials. The binding modes leading to the formation of dye-polymer conjugates can be either covalent or non-covalent (Figure 3). While the first approach obviously requires the formation of covalent bonds, non-covalent binding can occur through different kinds of interactions such as ionic and dipole-dipole interactions or through the formation of inclusion complexes.

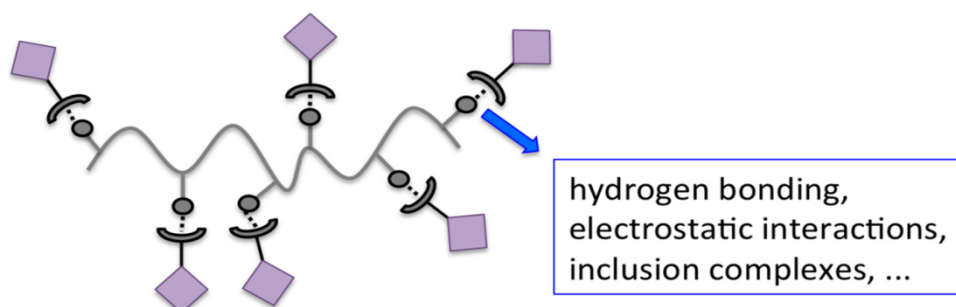


Figure 3 Schematic illustration of non-covalent dye binding to polymers (Adapted from Fleischmann et al, 2015).

Due to the large number of polar substituents that enable the formation of dipolar interactions with adequate substrates, sugar-based macromolecules are suitable materials for the supramolecular attachment of dyes. Such oligo-/polysaccharides can be obtained from natural products (e.g., starch, cellulose, chitosane) or from chemical linkage of monomeric subunits and are therefore readily accessible. The efficient adsorption of anionic azo dyes bearing sulfonate moieties to starch and β -cyclodextrin polymers was reported (Ozmen, E.Y et al, 2008). In the underlying studies, the polymers were prepared by crosslinking of β -cyclodextrin and starch, respectively, with hexamethylene diisocyanate. For both types of polymers, the main effects resulting in adsorption of the dyes were found to be hydrogen bonds formed between hydroxyl and amine groups located at polymers and the sulfonate moieties of the azo dyes. Additionally, cyclodextrins are known to form inclusion complexes with several azo dyes, and the formation of host guest complexes was therefore expected to contribute to the dye sorption of corresponding cyclodextrin-based polymers. The formation of such supramolecular complexes was verified, but a strong pH dependence was found and the whole effect was found to be inferior to the hydrogen bonding.

Besides the sugar-based materials discussed above, several other polymers were found to establish interactions with the dye molecules through ionic or dipole–dipole interactions. For instance, polymers formed via electrostatic self-assembly were described (Guan, Y.; et al, 2005). Fiber-like polymeric materials were formed from the combination of a positively charged perylenediimide derivative and a negatively charged copper-phthalocyanide derivative.

The impregnation of poly (methyl methacrylate) (PMMA) with the azo dyes Disperse Red 1 and Disperse Orange 25 solved in supercritical carbon dioxide was investigated in 2003 (Ngo, T.T. et al, 2003). Supercritical carbon dioxide serves as a good alternative for water in transporting the dye molecules, while acting as a swelling agent for the polymer at the same time. Adsorption of the dyes to the polymer was found to occur via hydrogen bonding or dipole–dipole interactions.

However, it was revealed that relatively strong dye–dye interactions hinder the diffusion process.

A solution to this problem was found by using a dye mixture. In that case, the intramolecular dye–dye interactions dominate the dye–polymer interactions, and accordingly, the diffusion rate is higher compared to the pure dyes. PMMA was employed for the non-covalent incorporation of dyes as well (Müller, M et al, 2000).

These methods can be considered as tailor-made solutions, once only specific colors can be added during the syntheses, meaning that the final user cannot formulate the color according to

his taste or requirements. Moreover, these products are usually developed for specific applications under high demanding performance conditions. (Broadbent et al, 2001, Zollinger et al, 1999).

3.1 Chemical systems considered as suitable for coatings production

Generally, the strategy adopted for developing polymeric dyes is usually to physically mix the dyes with polymeric matrices, where ionic bonds, hydrogen bonds or Van der Waals forces are expected to be established, depending on the used dyes. However, there is a thorny problem that, with time elapsing, the dyes may migrate and aggregate, leading to color fading of materials due to the noncovalent bond interaction between matrices and dyes.

Moreover, plenty of black dyes containing benzidine groups have a potential risk to humans and environment. Therefore, low-toxic and environmentally friendly alternatives are of great importance. (Wang et al, 2008).

An effective method to solve the problem is to chemically link the synthetic dyes to polymeric main chains (Alemdaroglu, F.E et al, 2009) or side chains (Tang, B et al, 2006) by various chemical reactions, being currently named as polymeric dyes. Generally speaking, polymeric dyes are safe and nontoxic for humans because they cannot be absorbed by skin owing to their large molecular dimension, excellent chemical and thermal stability. Moreover, polymeric dyes with tunable molecular structures exhibit great compatibility and strong binding force within the polymer chemical structure. In the past decades, many researchers have been devoted to the research about polymeric dyes. For example, in the 1980s, Marechal et al. studied systemically on polymeric dyes for the first time (Marechal, E et al, 1980, Libert, C et al, 1980).

Recently, many polymeric dyes have been prepared by incorporating chromophore groups (the molecular group that imparts color to the compound) into common polymeric materials, such as polyacrylates, polyethylene and polyamide, in order to enlarge the application fields (Deng, Y, et al, 2013).

Waterborne polyurethanes (WPU) as a kind of highly versatile polymeric material with excellent environment-friendly and low-toxic properties have been widely used as coatings, leathers, adhesives, and paints (Zhou, C et al, 2015). By a facile polycondensation reaction, a lot of colored WPU are developed by chemically incorporating the dyes into polyurethane matrices (Mao, H et al, 2015). As example, a series of novel black WPU dyes with different ratios of black dye, Sudan Black B, were prepared by a polycondensation reaction, resulting in films with

good migration and heat resistance, storage stability, while, at the same time, not causing significant aggregation or separation between the dye and the WPU matrices. Besides, Black WPU with different polymeric diols was also investigated, in order to develop black metal coatings, with excellent performance.

3.2 Examples of typical formulations of coatings

Considering the WBPU synthesis, up to date, most of the raw materials (polyols, isocyanates and chain extenders) are derived from petrochemical feedstock (Alam et al., 2014; Zhu et al., 2016).

With the depletion of the world crude oil stock and increasing environmental concerns, efforts on a global scale are dedicated to find a renewable resource (such as cellulose, natural oils, lignin, and so on) for bio-based polyurethanes to replace petroleum-based counterparts (Gaikwad et al., 2015; Zhang et al., 2014).

Vegetable oils as a kind of typical renewable biomass resources are among the most promising for polyol synthesis due to its low cost, and readily available (Pawar et al., 2015). Vegetable oils are triglyceride of fatty acid that usually bears 12–22 carbon atoms and 0–3 carbon–carbon double bonds. Except for castor oil, most vegetable oils do not contain hydroxyl groups (Gurunathan et al., 2015). The reactive ester and carbon–carbon double bonds in triglyceride oils offer several routes to introduce hydroxyl groups necessary in polyols for PU synthesis, including epoxidation/ring opening, ozonolysis/reduction, hydroformylation/reduction, transesterification, thiol-ene click reactions (Bullermann et al., 2013; Feng et al., 2017; Zhang et al., 2013). According to Zhang and co-workers, anionic and cationic PU dispersions have been synthesized from different vegetable oil-based polyols. It is found that the hydrophobic nature of triglycerides and long fatty acid chains endow PU films excellent chemical and physical properties, including enhanced hydrolytic stability, flexibility and toughness (Zhang et al., 2017). Lu et al. successfully prepared soybean oil-based cationic waterborne PU films with tensile strengths from 5.7 to 23.2 MPa and elongation at break from 235 to 291%. Moreover, the effect of polyols functionalities on the size of the polyurethane particle and the thermo-mechanical properties of the PU films were studied and discussed (Lu and Larock, 2010).

Fu and his co-worker synthesized a castor oil-based anionic waterborne PU film with a high flexibility (1 mm) and excellent chemical resistance (1.75% water absorption and 90% toluene absorption for 168 h) (Fu et al., 2014). Saalah et al. investigated the effect of the OH number,

DMPA content and hard segment content on the stability of the anionic waterborne PU dispersions from jatropha oil, as well as the physical, mechanical and thermal properties of the resulting films. The resulting PU film exhibited excellent hydrophobicity, with a contact angle of 90° or more, indicating a nonwetting surface (Saalah et al., 2015).

Considering the dyes incorporation, a series of polymeric dyes have been synthesized using anthraquinone and azo dyes as chromophores and epoxy, polyurethane, and polyvinylamine as polymer skeletons, to overcome the limitations of the original dyes. For example, the new polymerizable anthraquinone dyes were employed as comonomers and reacted with styrene, butyl acrylate and methacrylic acid via the semicontinuous emulsion copolymerization to prepare red and yellow polymer latexes (B. Li et al, 2012).

The resultant films exhibited better light fastness than the non-covalently colored latex films. In another study the stilbene chromophore and azo carboxyl diol were separately introduced into polyurethane chains to obtain polyurethane cationomers/anionomers. The resultant polyurethane exhibited good film-forming ability and their chemical structure can be photochemically induced to a high level upon UV light exposure (Buruiana, et al, 2001). Nevertheless, most of polyurethane polymeric dyes are based on covalent bonding by fluorescent dyes in relation to fluorescence investigations and photoelectric materials (D. W. Kim, et al, 2002).

The anthraquinone polyurethane have good adhesion to polymeric and glass surfaces and good film forming ability. A dyed silicon-containing anionic waterborne polyurethane was synthesized via grafting a reactive dye into a waterborne PU polymer, which displayed lower dye migration and greater light fastness (Wang et al, 2003). However, reactive dyes usually show complicated structures which limit their reactivity towards the terminal isocyanate groups of the prepolymer, leading to their low concentration in the final PU.

4 *Synthetic vs natural dyes*

Natural dyes can be extracted from plants leaves, fruits, vegetables, and flowers or from insects, bacteria and fungi (Fleischmann, C, et al, 2015).

Additionally, since time immemorial human beings have associated product qualities with their colors, this is especially true for meals. Historically, at the beginning of the food industry, the consumers were not worried about the nature of the dyes used in food coloring (natural or synthetic), but recently people have shown concerns related with these coloring agents.

Based on this framework, the use of natural dyes can be considered as a viable route to develop friendly alternatives. Natural dyes are derived from plants, animal, or mineral sources without any synthetic chemical treatment. One of the great parts of the natural dyes is vegetable-based being extracted from roots, berries, bark, leaves, and wood. Some filamentous fungi strains are also dye producers.

However, the main disadvantages of using natural dyes is related with their low stability under pH or temperature variations, depending on their groups. The natural dyes can be divided into four groups, according to the contained colouring substances: betalains, anthocyanins, carotenoids and carminic acid. Betalains are dyes with good stability under different pH values, presenting however a low thermal stability. Anthocyanins are highly unstable when subjected at pH variation, once their color varies from purple at acid pH to blue at pH around 10. Carotenoids have a good stability under pH variation from acidic to basic, having a low thermal stability. Carminic acid is, in its turn, stable under temperature variation and unstable under pH variation. Regarding the nature, carotenoids are hydrophobic compounds while betalains, anthocyanins and carminic acid are hydrophilic compounds. Considering the application of these dyes into WBPU coatings formulations, only the hydrophilic compounds can be considered as being an alternative.

5 Coating characterization methodologies

The variety of physical and chemical properties of coatings is determined by evaluating their thickness, structure and chemical composition. A fundamental understanding of coating properties requires a good knowledge of these parameters. Properties such as chemical structure can be evaluated by Fourier Transform Infrared Spectroscopy (FTIR) where contributions from the polymer and the dye chemical structure can be identified.

Thermal characterization is useful to understand the effect of the dye addition onto the polymeric film thermal behavior, with particular interest, when these materials are intended to be used under heat exposure. Moreover, the molecular weight analysis can be also important as it can be related with the mechanical resistance. Other properties like dye migration after the coating exposure under specific ambient conditions can be also useful for preview their behavior under real conditions application.

Regarding the evaluation of the dye effect on the coating color, colorimetric assays can be made, in order to evaluate the color variation according the dye concentration. Here, the color of each sample can be compared with a base coating without dye; this analysis is made by using a colorimeter. This can be done based on the CIELAB (also known as **CIE L*a*b*** or sometimes abbreviated as simply "Lab" color space) color space specifications (Velmurugan, P., et al, 2010)

The 1976 formula is the first formula that related a measured color difference to a known set of CIELAB coordinates. This formula has been succeeded by the 1994 and 2000 formulas because the CIELAB space turned out to be not as perceptually uniform as intended, especially in the saturated regions. This means that this formula rates these colors too highly as opposed to other colors. Given two colors in CIELAB color space, their comparison can be made according to equation (1):

$$\Delta E = \sqrt{\Delta l^2 + \Delta a^2 + \Delta b^2} \quad (1)$$



MATERIALS AND METHOD

6 *Materials and Methods*

Materials

PUD synthesis process

The PUD dispersion was synthesized using a propylene glycol polyol with molecular weight of 2000 (PPG 2000) supplied by DOW chemical company (Midland, Michigan, USA). The internal emulsifier dimethylol propionic acid (DMPA) and the neutralizing agent triethylamine (TEA) were both supplied by Fluka (Milwaukee, USA). Isophorone diisocyanate (IPDI) was supplied by Alfa Aesar (Karlsruhe, Germany) and dry acetone was used as solvent, while 1,2-ethylene diamine (EDA) was the chain extender, being both supplied by Panreac (Barcelona, Spain). Toluene from analytical grade and the catalyst tin (II) 2-ethylhexanoate (SO) were purchased from Sigma-Aldrich (St. Louis, USA). 2-propanol was obtained from Honeywell (Germany), *n*-dibutylamine (DBA) and bromophenol blue were purchased from Riedel-deHaën (Seelze, Germany). The spirulina bleu and carminic acid dyes were kindly offered by ADM Wild Europe GmbH.

Methods

Synthesis of waterborne polyurethane dispersion

Waterborne polyurethane dispersions were synthesized using the modified prepolymer method, developed by Fernandes and co-workers (2017). The prepolymer synthesis was done at a scale of 100 g using a reactor previously designed for this purpose by the LSRE-LCM group (Figure 4). This system is composed by a 500 ml glass vessel and is equipped with a temperature, stirring and reactant's addition control, and pH monitoring.

The first stage of this procedure corresponded to the prepolymer synthesis, where the IPDI, the polyether-based polyol (PPG2000) and catalyst (SO) were put into the reactor and stirred at 200 rpm, being heated at 80°C in order to start the prepolymer synthesis. During the reaction, the *n*-dibutylamine back-titration method was used for the NCO conversion (Appendix A). When the theoretical NCO conversion was reached, the reactor was cooled down to 50 °C in order to allow the addition of the pre-neutralized DMPA in acetone solution. This former was prepared by partially dissolving the DMPA (5%, w/w, pre-polymer basis) in 20 ml of dry acetone, under stirring, being TEA then added. After feeding this solution to the synthesis reactor, the reaction was maintained until the theoretical conversion to the NCO (typically 0.60) was reached. The

next stage corresponded to the dispersion of the prepolymer in water, at 25 °C. In this stage, the water was added at controlled flow rate under stirring at 500 rpm, being the total used volume 100 ml. If viscosity constrains were noticed during the phase inversion process, more acetone was added to dilute the medium. The obtained dispersion was heated to 35°C and the stirring rate was decreased to 200 rpm.

Then, the chain extension was made by adding an EDA aqueous solution (total volume of 25 ml) at a flow rate of 0.505 ml/min, being the amount of EDA calculated based on the NCO conversion achieved after the dispersion stage. This reaction was maintained during 2 hours, in order to promote the reaction of the NCO groups with the amine (NH₂) groups of EDA. Finally, acetone was removed in a rotary (Buchi Rotavapor R114 (Flawil, Switzerland)) evaporator at 50°C and 300 mbar, thus obtaining a dispersion with a solids content of around 35-40 wt%.



Figure 4 Reactor designed by the LSRE-LCM group for the synthesis of aqueous polyurethane dispersion.

Dispersion characterization

Dispersions were characterized in what concerns solids content, pH, particle size and viscosity.

- *Solid content determination*

The solid content of the PUD was determined through the procedure described in the standard EN 827:1996. In this procedure a sample of around 1 g of dispersion was weighted before and after being dried in an oven at 100 °C for 1 h, in duplicate. At the end of this period, the sample was placed in a desiccator until it was cooled to ambient temperature, being then weighed at intervals of 30 minutes until 3 consecutive values with a difference of less than 2 mg was obtained. The residual mass of the last weighing (m_f) is related with the initial mass according to Equation 2

$$\text{solid content (\%)} = \frac{m_f}{m_i} \times 100 \quad (2)$$

- ***pH determination***

The pH of the PUD depends directly on the free amine content in the dispersion. High pH values indicate the presence of unreacted amine exists in the dispersion. For this reason, the value of pH should be in the 7-8 range. The pH of the dispersion was measured according to with EN 1245: 1998, and the pH electrode (WTW, Weilheim, Germany) was calibrated using the standard solutions (4.01, 7.00) placed into the dispersion kept under stirring. The pH was registered when a constant value was achieved during 2 minutes (Fernandes, I.P, 2008).

- ***Viscosity determination***

The viscosity measurement is performed according to the procedure described in European standard EN 12092: 2001 using spindle used was TL5 (which requires a sample volume of 8 ml). The viscosities of the PUD were measured using a Visco Star Fungilab Brookfield viscometer (Barcelona, Spain) equipped with an Electro Temp heating/cooling bath to ensure a constant temperature during the measurement. The viscosity of the PUD is directly dependent on the particle size and influences the product handling and film-forming capacity, thereby affecting the performance of the product in the final application. For this reason, the viscosity of PUD varies in wide ranges, depending on the application for which they are intended. The suitable shear rate should be chose based on the equipment % EOS (viscometer parameter), which must be above 85%. When the measurement is complete, the viscometer has been stopped and left at equilibrium before a new measurement. The measurement is repeated for the same

sample until there are no more differences between two consecutive measurements greater than 3%.

- **The PUD particle size distributions**

The PUD particle size distributions (in number and volume) were measured by using a Malvern Mastersizer 3000 laser diffraction apparatus, equipped with a Hydro MV dispersion unit (Malvern, UK), using water as solvent. The obtained data was registered with Mastersizer software version 3.10. The results are presented as average values from five measurements.

Dyes incorporation into the PUD

Coating production through solvent casting

Spirulina blue (Figure 5) or carminic acid (Figure 6) were selected as hydrophilic dyes for coatings production. Both dyes were supplied in powder form, containing maltodextrin as drying agent, being the dye content of 18.0% for spirulina blue and 11.50% for carminic acid. PUD films with dye contents of 0.2, 0.5, 1.0, 1.5 and 2.0% ($w_{\text{dye}}/w_{\text{PU}}$), separately for each dye, were prepared in duplicated. Base films from PUD and dyed films with carminic acid and spirulina blue were prepared by solvent-casting. Briefly, 15 ml of the PUD were added to a beaker. Then the required amount of dye, according to the information described in Table 3, was added to the PUD and the mixture was left under stirring using a magnetic plate until the dye was completely dissolved. After, this mixture was poured into a Teflon mold and allowed to dry at room temperature during 1 week. Finally, films were dried at 60°C under reduced pressure (0.4 bar) for 1 day. The base films were produced by pouring the PUD directly into the mold, being after dried under the same conditions. The films were then stored in a desiccator before characterization. Waterborne polyurethane samples were coded as X% Spirulina blue or Carminic acid, where X referred to Spirulina weight content in the polyurethane dispersion, like for example 0.2%Sp.



Figure 5 Spirulina blue dye in powder form.

Table 2 Spirulina Blue (Sp) and Carminic acid (Cr) dyes contents added to the PUD films.

Dye content (%)	Sp mass (g)	Cr mass (g)
0.2	0.013	0.014
0.5	0.034	0.035
1.0	0.066	0.070
1.5	0.100	0.110
2.0	0.130	0.140



Figure 6 Carminic acid dye in powder form

Film characterization

Differential Scanning Calorimetry Differential Scanning Calorimetry (DSC) analysis were performed using a DSC 204 F1 Phoenix equipment from Netzsch (Figure 7). Aluminum pans

containing 7-11 mg of sample film were heated from -80°C to 250°C under nitrogen atmosphere. The heating rate was 10°C/min.



Figure 7 Differential Scanning Calorimeter, DSC 204 F1 Phoenix.

Colorimetry analysis

Colorimetric analysis was carried out using a CHROMA METER CR-400 from Konica Minolta, shown in Figure 8. This method allows the evaluation of color between samples. The color variation (ΔE) measured color difference based on the CIELAB coordinates and is calculated using the Equation (1):

$$\Delta E = \sqrt{\Delta l^2 + \Delta a^2 + \Delta b^2} \quad (1)$$

Where: ΔL , Δa and Δb values provide a complete numerical description of the color differences between a reference or standard and a sample ΔL represents a lightness difference between sample and the standard.

- Δa represents a redness or greenness difference between the sample and the standard.
 Δb represents blueness-yellowness difference between the sample and the standard.



Figure 8 CHROMA METER CR-400 from Konica Minolta used to measure the color of films.

Fourier Transform Infrared Spectroscopy (FTIR)

The analysis of the films chemical structure was made by Fourier Transform infrared spectroscopy (FTIR) using a MB3000 spectrometer from on ABB Inc operating in ATR mode (ATR cell equipped with a diamond crystal). The spectra acquisition was made by co-adding 32 scans, with a resolution of 16 cm^{-1} , between $4000\text{-}550\text{ cm}^{-1}$, using the software Horizon MB v.3.4. Baseline correction was performed.



Figure 9 Fourier Transform Infrared (FTIR) equipment used to the analyze the films chemical structure



RESULTS AND DISCUSSION

7 Results and discussion

The production of the eco-coatings based on natural dyes and polyurethane aqueous dispersions (PUD) was divided in three sequential stages:

1. PUD production through the modified prepolymer method. Here 4 synthesis assays were done in order to obtain 1L of dispersion. After the PUD properties (in dispersion form) were evaluated, by measuring the viscosity, solids contents, pH and particle size;

2. Eco-coatings production and films characterization. Films of PUD alone and with added carminic acid and spirulina blue dyes were produced by solvent casting. Then the films were characterized in terms of chemical structure (FTIR) and thermal properties (DSC) and thermal stability (TGA) in order to evaluate the influence of the dyes on these properties. In addition, the color variation generated by the different dyes incorporation comparatively with the base PUD coating (without dyes) was measured.

7.1 PUD characterization

The solid content, pH and viscosity determined for the PUD (Figure 10) are described in Table 5. Regarding the pH a value of 7.37 was measured, being a typical value that confirms the success of the chain extension step, once the presence of free EDA will result in the pH increment (Fernandes, 2017; Santamaria Echart, 2017). In the case of the viscosity the mean value obtained was 177.52 mPa.s, being dependent of the dispersion particle, where lower sizes give higher viscosity values due to the increase of the particles interaction while larger sizes result in lower viscosity (Fernandes, 2017). With respect to the solids content, the value of 39.2% obtained is close to the commercial products in general. This solid content was expected, once the dispersion synthesis was made in order to maximize this content without impair the dispersion stability (Palloma, et al, 2018).



Figure 10 Typical white color of the produced PUD.

Sample	pH	Viscosity (mPa.s)*	Solid content (% , m/m)
PUB	7.37	177.52	39.23

Table 3 Values of pH, viscosity and solids content obtained for the PUD.

Particle size distribution

The particle size distributions in volume and number of the PUD are shown in Figure 10. The mean values of the D10 D50 and D90 percentiles are described in Table 6.

Analyzing the PUD particle size distribution in volume (Figure 11 (a)), and in number distribution (Figure 11 (b)) two unimodal patterns were identified, being typical from this type of products (Fernandes, 2017). The mean particle size based on the volume distribution is 1.15 μm (D50 mean value), while the obtained from the number distribution is 0.801 μm . These results are related with the internal emulsifier (DMPA) content (5%, w/w) used on this dispersion, which usually lead to products with mean particle sizes lower than 10 μm (Son et al., 1998).

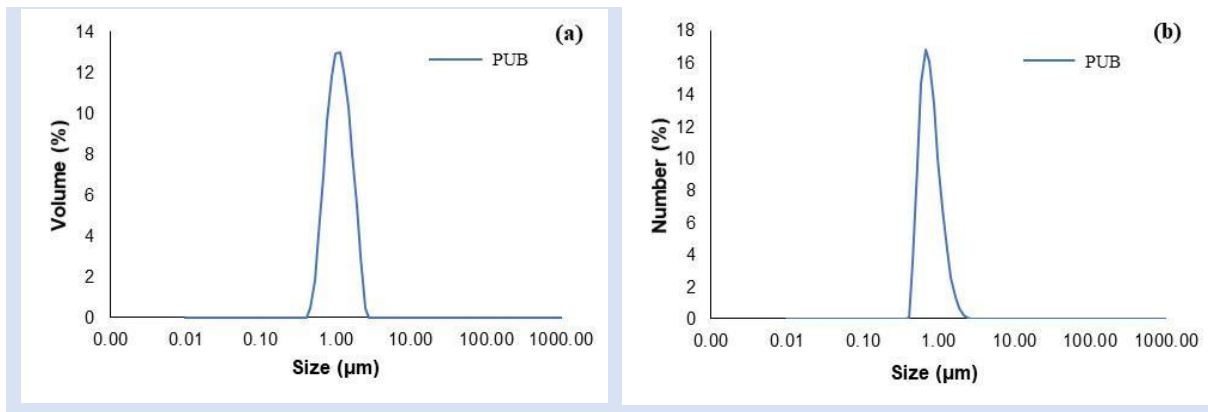


Figure 11 Particle size distributions of PUD sample: (a) volume distribution and (b) number distribution.

Sample	Volume distribution			Number distribution		
	D ₁₀ (μm)	D ₅₀ (μm)	D ₉₀ (μm)	D ₁₀ (μm)	D ₅₀ (μm)	D ₉₀ (μm)
PUD	0.722 ± 2.1x10⁻⁴	1.150 ± 2.5x 10⁻⁴	1.840 ± 3.0x 10⁻⁴	0.570 ± 2.1x 10⁻⁴	0.801 ± 2.6x 10⁻⁴	1.260 ± 3.0x 10⁻⁴

Table 4 Values of D10, D50, and D90 obtained from volume number distributions of the PUD sample.

7.2 PUD films characterization

Analyzing the appearance of the films, which is shown in Figure 12 and 13, some remarkable differences can be noticed being related with the amount of dye incorporated. For PUD, a transparent film was obtained, being a typical aspect of this type of films. With the Spirulina dye incorporation, the films became bluer as the dye content increased from 0.2 to 2.0%. For the films produced with carminic acid a similar behavior was identified once the films became redish with the dye increment, meaning that the dye increase on the formulations results in the color intensification of the coating films.

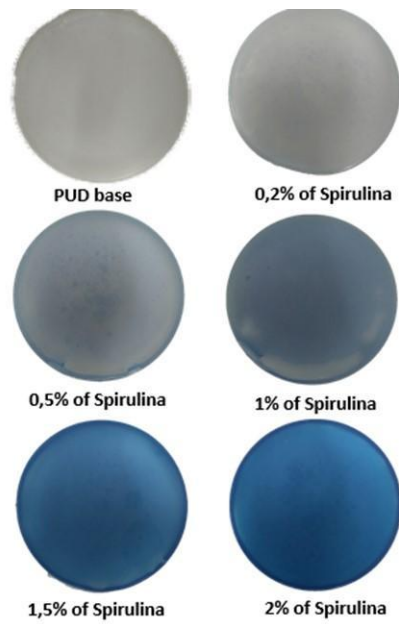


Figure 12 PUD films with different amount of Spirulina dye obtained after drying

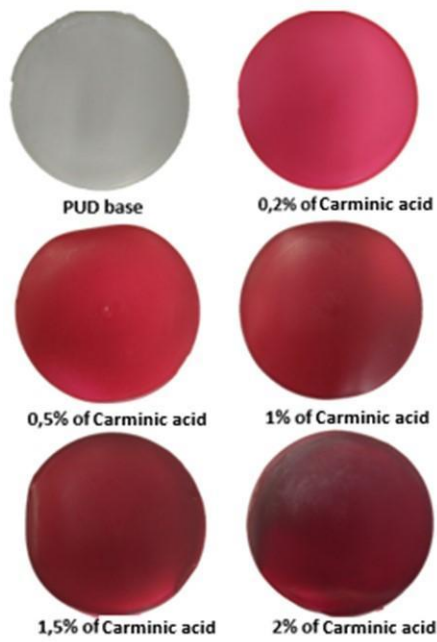


Figure 13 PUD films with different amount of Carminic acid obtained after drying.

Considering the FTIR analysis, the spectra of PUD and Spirulina blue dyed PUD films and Carminic acid films are shown in Figure 14 and 15, respectively. The analysis of the Spirulina spectra shows a vibration centered at 3390 cm^{-1} that is related with the OH groups from phycocyanin (chromophore group) and maltodextrin, together with the contribution of the phycocyanin's NH groups. The C=O from acid groups and NH stretching from amides II groups vibrations, both from phycocyanin, were identified at 1651 and 1542 cm^{-1} . The presence of maltodextrin is identified due to the vibration centered at 1006 cm^{-1} , being assigned to its polysaccharide's structures.

Considering the spectra of the pure PUD film, the following features can be assigned: the vibration detected between $3500\text{-}3100\text{ cm}^{-1}$ correspond to N-H of urethane and urea groups, while the peak around 1720 cm^{-1} is assigned to the C=O vibrations of the urethane, urea and DMPA acid groups (Santamaria Echart, 2017; Tsou et al., 2017). Moreover, the prominent peak identified between $1300\text{-}1000\text{ cm}^{-1}$ is attributed to the C-O vibration from PPG ether group. Additionally, the non-appearance of the vibration at 2270 cm^{-1} indicates the absence of the NCO groups, proving its complete conversion during the synthesis process. Analyzing the carminic acid FTIR spectra (Figure 15) the presence the OH vibration at 3390 cm^{-1} due to the contribution of both the carminic acid and maltodextrin is identified, together with the C=O and C=C vibrations both from anthraquinone structure, noticed at 1643 cm^{-1} and 1552 cm^{-1} , respectively. The peak at 1006 cm^{-1} is due to the polysaccharide structures of maltodextrin. Analyzing the spirulina dyed films, no major contributions of the dye can be observed on the film's spectra, meaning that the dye is not chemically bound to the PUD structure. Also, the amounts of dye added are not enough to have significant contribution on the film spectra. For carminic acid films, the same behavior is identified.

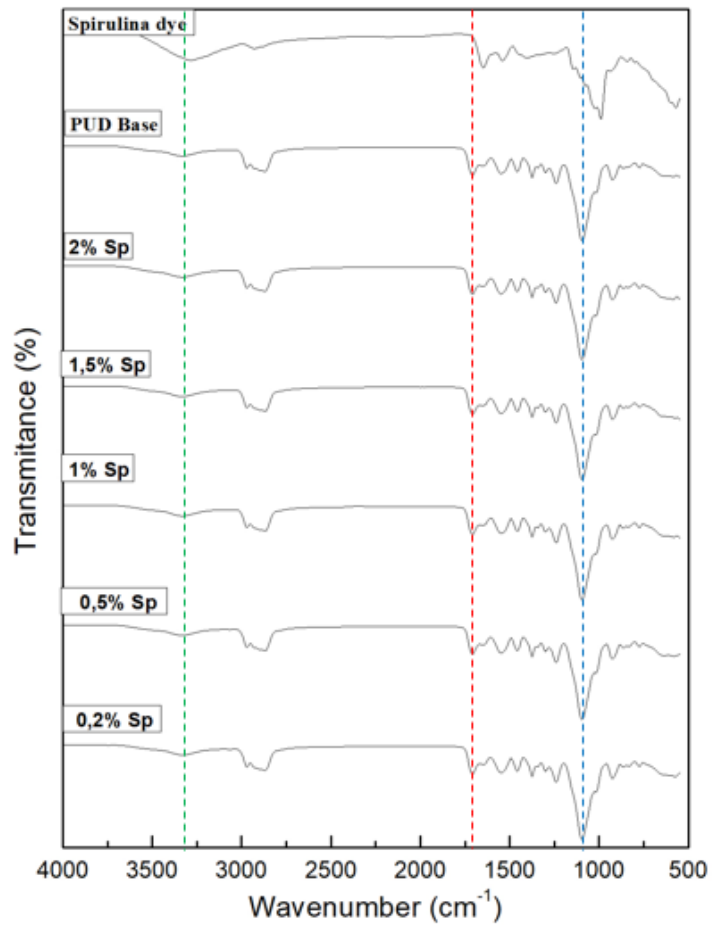


Figure 14 FTIR spectra of Spirulina dye, PUD film and PUD films added with 0.2, 0.5, 1.0, 1.5 and 2.0% of Spirulina dye

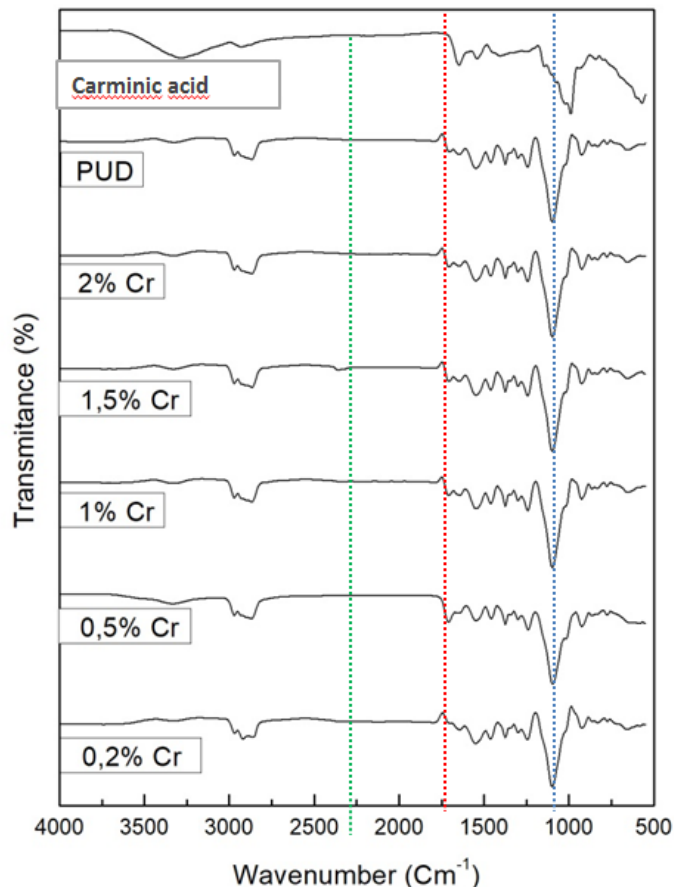


Figure 15 FTIR spectra of Carminic acid dye, PUD film and PUD films added with 0.2, 0.5, 1.0, 1.5 and 2.0% of carminic acid dye.

Differential scanning calorimetry

The thermal behavior of PUD film and films added with the different contents of the dyes was evaluated by differential scanning calorimetry (DSC) being the obtained thermograms shown in Figure 16 and 17. The glass transition temperature (T_g), melting temperature (T_m) and melting enthalpy variation (ΔH_m) of Spirulina and Carminic acid films are summarized in Table 8 and 9 respectively.

Looking to the values to the PUD base film, the values of T_g and T_m were -52.0°C and 99.1°C , respectively, while the enthalpy of 27.82 Jg^{-1} was registered. For the films containing 0.2, 0.5, 1, 1.5 and 2% of both Spirulina blue and carminic acid, the T_g values were equal to the obtained for the PUB, meaning that no differences of the thermal behavior at low temperatures was achieved due to the dye incorporation. However, regarding the T_m values of the carminic acid films a

diminution for 94.0 and 90.7°C was registered for the 0.2 and 0.5%Cr samples, comparatively to the PUD film. In addition, a decrease from 97.0 to 94.3 was noticed for the samples 1.0 e 1.5%Cr, while for 2%Cr the T_m value increased again for 98.5°C, being near to the one obtained for the PUB sample. For ΔH_m , the value registered for PUD film was 27.82 Jg⁻¹. For the dyed films different patterns were found, depending on the amount and type of dye. For 0.2%Sp an increase of ΔH_m to 28.30 Jg⁻¹, comparatively with the PUD film. However, as the dye content increased from 0.2% to 1.5%, the ΔH_m decreased until 24.33 Jg⁻¹, increasing again until 31.40 Jg⁻¹ for the 2.0%Sp sample. For carminic acid the ΔH_m value was 23.4 Jg⁻¹, decreasing to a minimum value of 21.28 Jg⁻¹ for the 0.5%Cr sample. After, ΔH_m increased as the dye content increased until the maximum value of 36.48 Jg⁻¹ was reached for 2%Cr. Analyzing these results it can be seen that both the T_m and the ΔH_m values lowered until a minimum value when the dye content was 1.5%, being probably related with the dye distribution on the PUD molecular structure rearrangement, interfering with the hard segments organization, leading to a decrease of both the T_m and ΔH_m , comparatively with the base PUD. However, when the dye amount was increased till 2%, an increment of both T_m and ΔH_m was noticed, which might be attributed to the favoring of the hard segments rearrangement, leading to more organized structures that will result in both T_m and ΔH_m increase. These observations are in good agreement with the findings of Santamaria-Echart and co-workers (2018) for other natural additives.

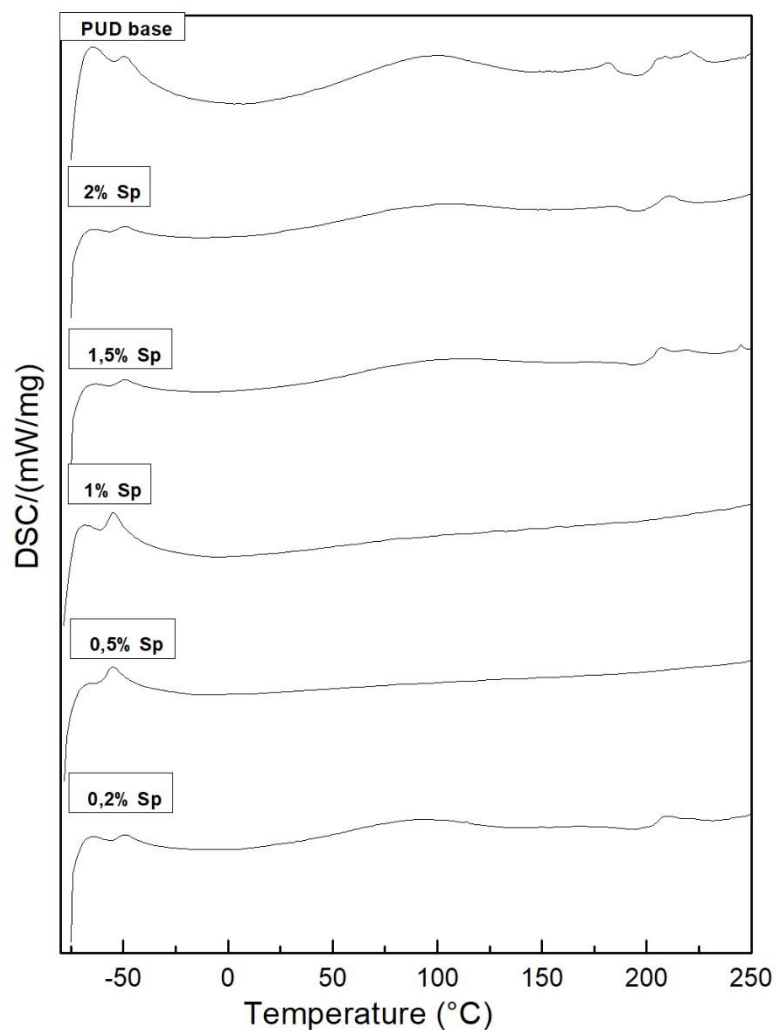


Figure 16 DSC thermograms of PUD film and PUD films added with 0.2, 0.5, 1.0, 1.5 and 2.0% of Spirulina dye.

Table 5 Thermal properties of PUD film and PUD films added with 0.2, 0.5, 1.0, 1.5 and 2.0% of Spirulina blue.

Sample	T _g (°C)	T _m (°C)	ΔH _m (Jg ⁻¹)
PUD	-52.0	99.1	27.82
0.2% Sp	-52.2	94.1	28.30
0.5% Sp	-52.4	105.4	20.79
1.0% Sp	-52.7	95.3	21.70
1.5% Sp	-52.3	112.7	24.33
2.0% Sp	-52.2	104.5	31.40

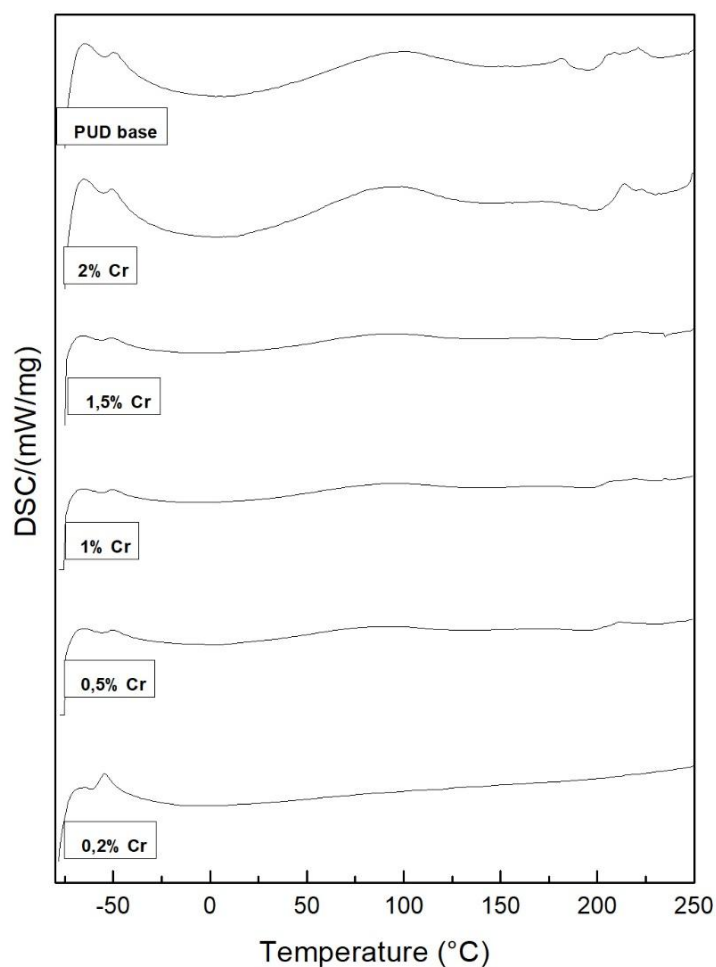


Figure 17 DSC thermograms of PUD film and PUD films added with 0.2, 0.5, 1.0, 1.5 and 2.0% of Carminic acid.

Table 6 Thermal properties of PUD film and PUD films added with 0.2, 0.5, 1.0, 1.5 and 2.0% of Carminic acid.

sample	T _g (°C)	T _m (°C)	ΔH _m (Jg ⁻¹)
PUD	-52.0	99.1	27.82
0.2%Cr	-53.8	94.0	23.46
0.5%Cr	-52.5	90.7	21.28
1.0%Cr	-52.9	97.0	23.76
1.5%Cr	-52.8	94.3	22.94
2.0%Cr	-52.7	98.5	36.48

Thermogravimetric analysis

The TGA analysis was applied to evaluate the thermal stability of the dyes, the PUD film and the dyed films. The obtained results are registered in Table 9 and 10, while the TG and DTG curves are shown in Figure 20 and 21. Considering the Spirulina blue, two degradation stages are identified, where the first one occurs from 32 °C to 148 °C (mass loss 5.34%) was related with the water removal. Then, the second stage occurring between 148 to 419°C is due to the decomposition of phycocyanin and maltodextrin, corresponding to a mass loss of 54%. The final residue obtained at 750°C is was 16.3%.

Looking at the thermal degradation profile of the PUD film samples three main decomposition stages can be identified. Where the first degradation stage starts at 191°C, being related with the urethane group decomposition. Next, the second degradation stage starting at 278°C, correspond to the urea decomposition, while the third one starting at 341°C is related with the soft segment decomposition. This is a typical degradation pattern of water-based polyurethane, since two different hard segments were formed during the synthesis, due to the reaction of the polyol and the diamine with the NCO, resulting on the formation of urethane.

Analyzing the degradation pattern of the Spirulina blue dyed films, for 0.2%Sp sample, a displacement of the first and second degradation stages for higher temperatures is noted (maximum temperature of the PUB were 278 and 341°C, increasing to 274 and 324°C for the PUD 0.2%Sp, as it can be seen in Figure 18. This is also detected for the PUD 0.5%Sp, 1%Sp, 1.5%Sp and 2%Sp samples and can be related with the dye incorporation, which contains compounds able to increase the thermal stability of the polymer (López-de-Dicastillo et al., 2010; López-de-Dicastillo et al., 2011). The presence of the dye into the films is also visible through the residue obtained at 750°C, once for 2%Sp a final residue of 2.80%was registered, while for the PUB a total degradation was achieved at this temperature (Table 7).

☐ Carminic acid's films

Analyzing the Carminic acid TG degradation pattern present two main stages, where the first one comprised between 32 and 105 °C, is due to the loss of the free water contained together with the water adsorbed by the maltodextrin, representing a mass loss of 6.24%. The second degradation stage occurs from 105 to 408 °C (mass loss of 52%) being related with the carminic acid and maltodextrin degradation. However, here two degradation stages can be distinguished, where the

first one occurred at 277 and 408 °C is typical of the maltodextrin decomposition, and the second starting at 164 °C corresponds to the carminic acid degradation. The final residue obtained at 750 °C was 28.2%.

Looking at the thermal degradation profile of the carminic acid dyed film's 0.2%Cr, 0.5%Cr, 1%Cr, 1.5%Cr and 2%Cr, three main decomposition stages can be identified. Analyzing the degradation pattern of the PUD 0.2%Cr sample, a displacement of the first and second degradation stages for higher temperatures is noted (maximum temperature of the PUD film were 278 and 341°C, increasing to 274 and 324°C for the 0.2%Cr), as it can be seen in Figure 19. This is also detected for the PUD 0.5%Cr, 1%Cr, 1.5% Cr and 2%Cr samples and can be related with the dye incorporation, which contains compounds able to increase the thermal stability of the polymer (López-de-Dicastillo et al., 2010; López-de-Dicastillo et al., 2011). The presence of the carminic dye on the 0.2%Cr, 0.5%Cr and 1%Cr films is also visible through the residue obtained at 750°C, once for 2%Cr a final residue of 1.11% was obtained, while for the PUD film a total degradation was achieved at this temperature (Table 8).

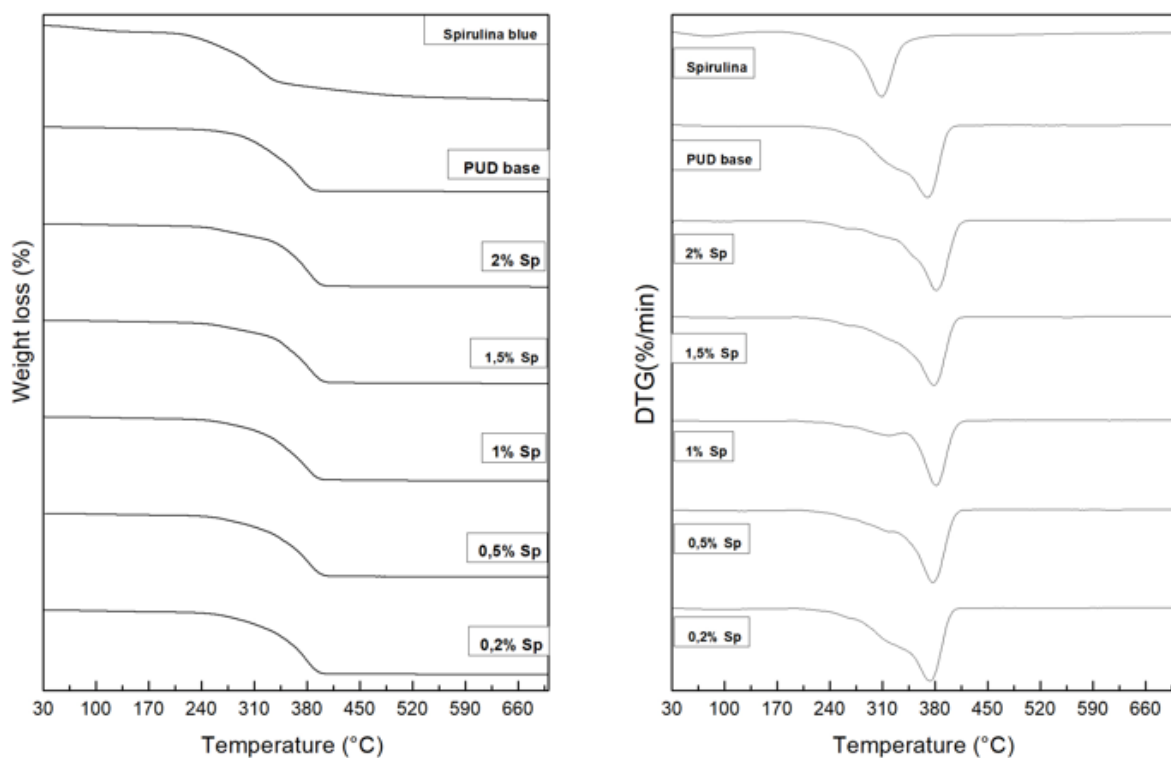


Figure 18 TG and DTG curves of the Spirulina dye, PUD film and Spirulina dyed films.

Table 7 Weight loss, initial (Ti), final (Tf) degradation temperatures, and residue at 750°C of the Spirulina dye, PUD film and Spirulina dyed films.

Sample	Residue	T _i (°C)	T _f	Weight loss (%)
Spirulina dye	16.32	148	419	63.26
		419	600	9.77
		600	750	5.13
PUB base	0.0	191	278	7.12
		278	341	36.47
		341	423	53.54
0.2%Sp	1.03	189	274	6.62
		274	326	22.49
		326	469	66.13
0.5%Sp	0.20	202	266	5.02
		266	326	19.72
		326	480	71.10
1%Sp	5.48	194	276	6.84
		276	338	19.99
		338	481	64.47
1.5%Sp	0.0	190	269	6.05
		269	333	22.59
		333	480	67.18
2%Sp	2.80	245	326	19.95
		326	358	19.64
		358	480	53.18

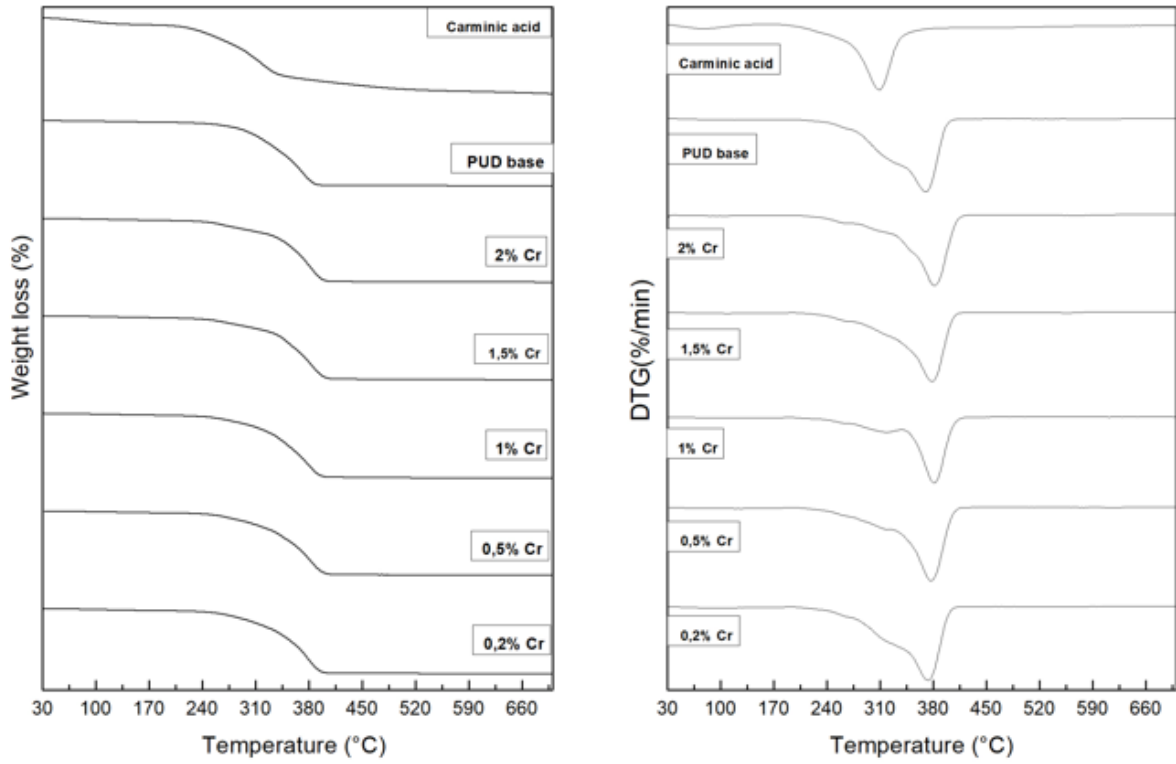


Figure 19 TG and DTG curves of the carminic acid, PUD film and carminic acid dyed films.

Table 8 Weight loss, initial (Ti), final (Tf) degradation temperatures, and residue obtained at 750°C for of the carminic acid, PUD film, and carminic acid dyed films.

Sample	Residue	T _i (°C)	T _f	Weight loss (%)
Carminic acid dye	28.22	105	276	16.9
		276	398	35.31
		398	750	13.16
PUB base	0.0	191	278	7.12
		278	341	36.47
		341	423	53.54
0.2%Cr	0.0	200	283	9.34
		283	319	13.08
		319	480	73.86
0.5%Cr	1.18	191	286	10.52
		286	345	25.54
		345	480	59.07
1%Cr	0.34	200	281	9.17
		281	348	32.46
		348	481	53.93
1.5%Cr	1.06	200	304	14.63
		304	357	27.26
		357	480	52.29
2%Cr	1.11	196	281	10.10
		281	355	28.79
		355	479	55.19

Colorimeter analysis

The color variation was measured by comparing the color of the PUD film with the dyed films. Each sample was measured in three different zones and the L, a and b values described correspond to an average value. The color coordinates and the respective variations values are detailed in Tables 9 and 10.

For spirulina blue and carminic acid film's color intensity varied according to the dye content added. It is known that ΔE values higher indicate that the color difference is visually appreciable. For Spirulina blue the color variation increase with the dye content rise, reaching a maximum value of 65.58 for 2%Sp, as it can be observed in Figure 18. However, for carminic acid, the color variation reaches a maximum value of 70.62 for 1.0%Cr, being constant for the higher dye content.

Table 9 Color coordinates and respective variation obtained for the PUD film and the films dyed with the tested spirulina contents.

Sample	L*	a*	b*	ΔL	ΔL^2	Δa	Δa^2	Δb	Δb^2	ΔE
PUD	86.50	-0.60	9.60	-	-	-	-	-	-	-
0.2%Sp	76.21	-0.47	3.50	-10.29	105.88	0.13	0.017	-6.10	37.21	11.9
0.5%Sp	65.36	-0.33	-6.37	-21.14	446.89	0.27	0.073	-15.80	255.04	26.5
1.0%Sp	54.37	2.02	-13.35	-32.13	1032.33	2.62	6.86	-22.30	526.70	39.5
1.5%Sp	46.78	3.11	-27.97	-39.72	1577.67	3.71	13.76	-37.60	1411.50	54.8
2.0%Sp	40.69	8.36	-36.46	-45.81	2098.55	8.96	80.28	-46.06	2121.52	65.5

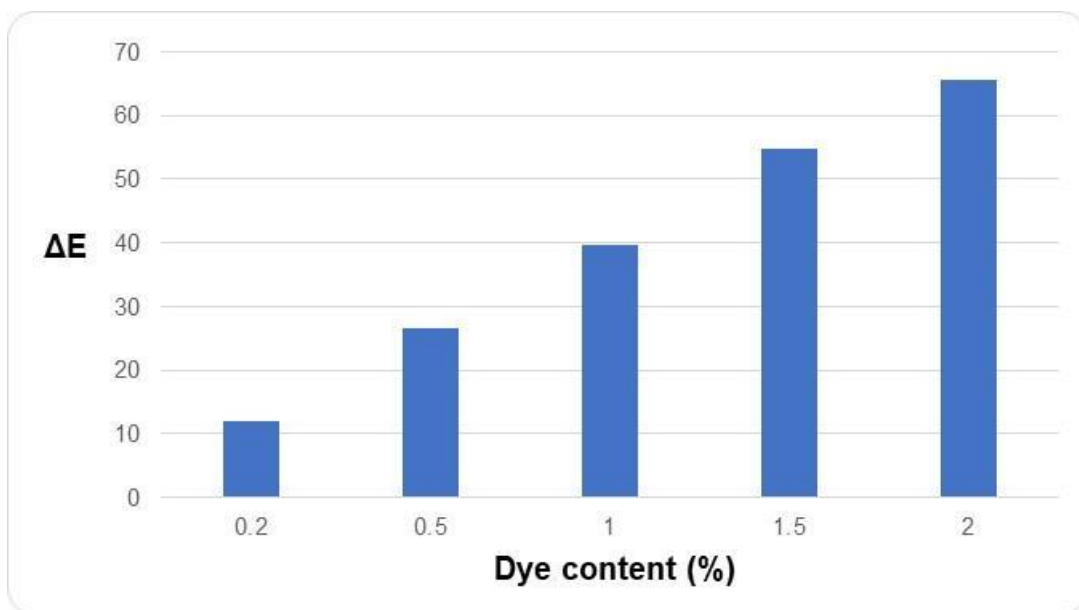


Figure 20 Color variation of the film's samples dyed with spirulina.

Sample	L*	a*	b*	ΔL	ΔL^2	Δa	Δa^2	Δb	Δb^2	ΔE
Control sample	86.50	-0.60	9.60	-	-	-	-	-	-	-
0.2%Cr	65.24	38.25	5.41	-21.26	451.99	38.85	1509.32	-4.19	17.55	44.48
0.5%Cr	35.94	44.66	21.66	-50.56	2556.31	45.26	2048.48	12.06	145.44	68.92
1.0%Cr	35.77	46.83	22.40	-50.73	2573.53	47.43	2249.60	12.80	163.84	70.62
1.5%Cr	34.76	45.49	20.93	-51.74	2677.02	46.09	2124.29	11.33	128.36	70.21
2.0%Cr	35.61	46.78	21.48	-50.89	2589.80	47.38	2244.90	11.88	141.13	70.54

Table 10 Color coordinates and respective variation obtained for the PUD film and the films dyed with the tested carminic acid contents.

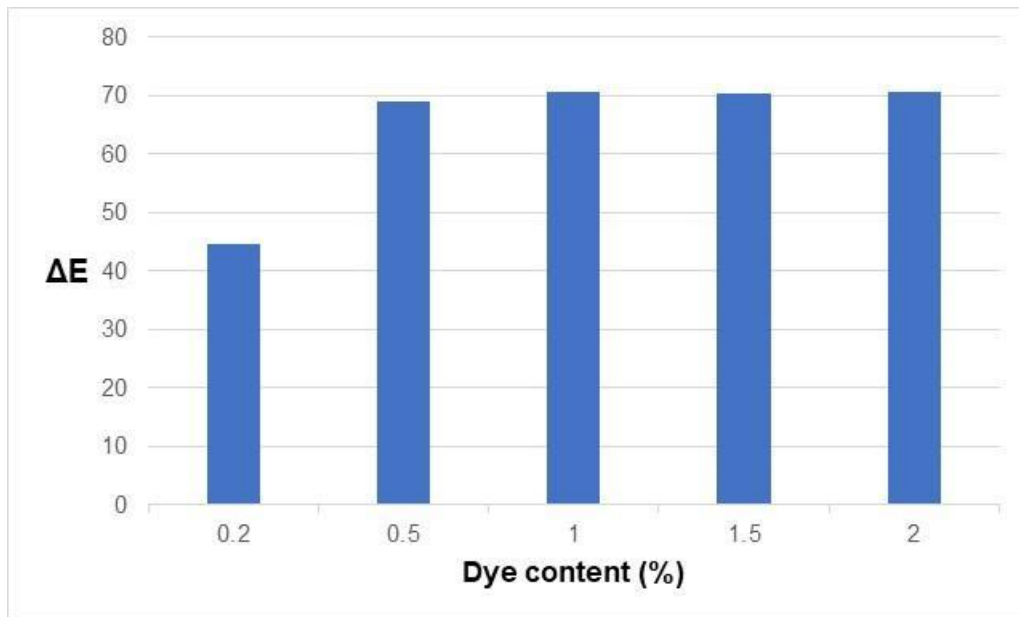


Figure 21 Color variation of the film's samples dyed with carminic acid.



CONCLUSION AND FUTURE

WORK

8 *Conclusion and Future Work*

The main objective of the present work is to study the production of bio and eco-coating with based on natural dyes and polyurethane aqueous dispersions. For this study a polyurethane aqueous dispersion based on PPG was synthesized. After the characterization of the dispersion properties, namely solids content, viscosity, pH and particle size. Typical values were obtained, namely: Solid content: 39.23, pH: 7.37, Viscosity: 177.52, and the mean particle size based on the volume distribution is 1.15 μm (D50 mean value), while the obtained from the number distribution is 0.801 μm . Afterwards coatings modified with carminic acid and spirulina blue dyes were produced by incorporating dyes contents of 0.2, 0.5, 1.0, 1.5 and 2.0% (w/w) into the PUD. After drying, dyed films were obtained and characterized. With respect to films characterization, the polyurethane chemical structure was confirmed through Fourier Transform Infrared Spectroscopy. Differential Scanning Calorimetry analysis confirmed the effect of the Dye (Spirulina or carminic acid) on the films thermal behavior, once when 2% of dyes were added, the values of melting temperature (T_m) and the melting enthalpy variation (ΔH_m) changed. This behavior was attributed to the dye interference with the hard segment rearrangement occurring at molecular level, comparatively with the one observed for PUB film. The thermogravimetric analysis showed an increase of the films thermal stability related with the incorporation of the dye. Regarding the color variation evaluation, by analyzing and comparing the PUD film color with the dyed films, an increasing of the color variation was detected for both dyes. However, for the films containing Spirulina blue the color variation increase with the dye content rise, reaching a maximum value of 65.58 for 2%Sp, but for carminic acid, the color variation reaches a maximum value of 70.62 for 1.0%Cr, being constant for the higher dye content.

As future work, it would be very interesting to study the antimicrobial activity of Spirulina and carminic acid dyed and produced films. It would be also important to study the influence of higher dyes content. It would be also interesting to do the evaluation of the film's mechanical properties. In addition, other strategies of incorporation should be tested, for example during the phase inversion stage of the PUD synthesis, in order to study the dyes, influence on the films thermal and mechanical properties.



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APPENDICES

Appendices

Appendix 1

Determination of the NCO content through Dibutylamine (DBA) method

The residual NCO groups were quantified according to the guidelines of the EN 1242:1993 standard. The adopted procedure can be described as follows:

1. Add 25 ml of toluene to 4 erlenmeyers with lids;
2. Add 6.3 ml of the dibutylamine/toluene solution (108 ml DBA + 400 ml toluene) were added to the erlenmeyers (v_A)
3. For each reaction time (15, 30, 45 min and after the dispersion production), approximately 2g of prepolymer were collected and weighted into each Erlenmeyer.
4. Next, the Erlenmeyer was kept under heating at 60°C during 5 minutes. Then, the sample solution was left to cool until ambient temperature under stirring.
5. Next, 50 ml of 2-propanol and 0.25 ml of bromophenol blue were added to the sample's solution before the titration with HCl 1N until a persistent yellow color appear.

A Blank sample was also prepared following the same procedure, without the sample addition. The NCO content was calculated and expressed as a percentage using Equation (1), where V_B is the volume of titrant consumed in the blank titration (ml), V_A is the volume of titrant consumed in the sample titration (ml), $NHCl$ is the concentration of the titrant solution expressed in normality (N), and m_A is the mass of the sample (g). The obtained NCO conversion is calculated by Equation (2):

$$NCO (\%) = \frac{(v_B - v_A) \times NHCl \times 4.2}{m_A} \quad (1)$$

$$\rho_{NCO} = \frac{(NCO)_i - (NCO)_f}{(NCO)_i} \quad (2)$$

Appendix 2

Table 1 Experimental records of the NCO groups obtained along the PUD synthesis

Reaction NCO:OH _{PPG}		Reaction NCO:OH _{DMPA}		After phase inversion	
Assay	Theoretical conversion	Experimental conversion	Theoretical conversion	Experimental conversion	Experimental conversion
1	0.28	0.33	0.29	0.29	0.70
2	0.29	0.30	0.29	-*	0.73
3	0.29	0.30	0.60	0.67	0.67

*values not available

Appendix 3

Abstract accepted for poster communication on the 10th Conference on Green Chemistry and Nanotechnologies in Polymeric Materials, to be held in Latvia in October 2019.



#

NEW ECO-COATINGS BASED ON NATURAL DYES AND AQUEOUS POLYURETHANE DISPERSIONS

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Coatings are polymeric materials used as protective and embellishment agents in several substrates, being expected to maintain the properties along time and under aggressive environments. In the context of coatings industry, the traditional solvent based coatings are being progressively replaced by water based products, like environmentally friendly aqueous polyurethane dispersions. From a final application perspective, e.g. in decorative applications, the coatings are usually formulated with synthetic dyes by post-mixing procedures. However, due to their low water compatibility, phase separation or agglomeration phenomena can occur. These issues can be surpassed by replacing these dyes by aqueous extracts with colorant power, which beyond having higher compatibility with water, might add some functional properties, such as antimicrobial and antioxidant power. These features can impart innovative properties to the coatings, namely increase the lifetime due to the reduction of the oxidative phenomena or by confer antimicrobial properties, beyond the coloring effect.

In this context, the present work is devoted to the development of new eco-coatings based on natural water compatible dyes and polyurethane aqueous dispersions (PUD), obtained by a NMP (N-methyl pyrrolidone) free method. Firstly, the PUD were synthesized by the modified pre-polymer process, using an NCO/OH ratio of 1.7 and a chemical system based on isophorone diisocyanate, polypropylene glycol (MW2000), dimethylol propionic acid as internal emulsifier, stannous octoate as catalyst, triethylamine as neutralizing agent, ethylene diamine as chain extender and dry acetone as solvent. Thereafter, the PUD pH, viscosity, solid content and particle size were measured. Phycocyanin and carminic acid were selected as water compatible natural dyes. Then, each dye was added to the PUD by the post-mixing process, being the amount tested 0.2, 0.5, 1.0, 1.5 and 2.0% (w_{dye}/w_{PUD}). After, coating films of the base PUD (base film), and films incorporating the dyes were produced by the solvent casting method. The films were dried under environmental conditions during one week, being followed by an additional drying using a vacuum oven at 45°C during 12 hours. Films were characterized in terms of chemical structure (FTIR), thermal behavior and stability (DSC/TG), color (colorimetry) and antimicrobial activity (agar diffusion method), and properties related with films composition.

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