Synthesis of High Performance Polyurethane Films

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Abstract

This paper deals with the formulation of a polyurethane paint with greater outside performance, through the use of UV protectors used in the polypropylene industry and polystyrene resin in low proportions. The manufacturing methodology is simple; it consists in a sequential mixing process under constant stirring. Thermal results indicated that the formulation works perfectly with a protective additive concentration of up to 1000ppm and 1% of polystyrene. Spectroscopic results showed high similarity compared to commercial paints. Thermal results displayed high thermal stability under 400ºC. Finally, performance tests showed values higher than those standardized by ASTM.

Keywords: Polyurethane paint, UV-protectors, polypropylene, Polystyrene, Spectroscopic, ASTM

INTRODUCTION

Since the Paleolithic era paintings have been used for decoration and protection. The Greeks and Romans first used lead carbonate "white lead", white pigment (toxic). The Egyptians and the Greeks made paints based on gum and wax with natural pigmentations such as iron oxide and carbon black. In the middle ages and the Renaissance there was a huge growth in artistic paints, while industrial paints had not been developed extensively, due to the lack of applicability. The first synthetic resins, as components of paints (nitrate and cellulose acetate) appeared during the First World War, and there are many components of paint that give it viscosity and plasticity in addition to other properties [1].

Paints are the most suitable method for the protection of the different materials used in construction and industry. A paint may be defined as a dispersed system of finely dispersed solids in a fluid medium which fulfills vehicle functions. This material is based on a binder substance, also called a film former or binder, immersed in a solvent, to which additives and plasticizers are added. In the case of organic solvent based paints, the carrier is a liquid solution (molecular dispersion of the polymeric material) suspending the pigment particles; during drying the system shows a significant volumetric shrinkage of the film [2-4].

In the field of paints hundreds of researchers stand out that work on the development and improvement of the same, among them we highlight:

In 1956, Reilly and Orchin prepared and reported the properties of films based on polyurethane polymers and studied their protection on aluminum surfaces [5].

In 1970, Koutsky et al studied the electron microscopic properties of polyether-urethane and polyester-urethane block copolymers, they concluded that the domain size may range from 3 to 20 nm and depends on the reactants used as well as the polymerization conditions [6].

In 1989, Chen et al. studied the chemical properties and applications of polyurethanes on metallic and plastic surfaces [7].

In 1988, Prime et al studied several applications of DMA and TGA to quality and process control in the manufacture of magnetic coatings. They concluded that thermo-degradation behavior of PUs at high temperatures provides a fingerprint of the material that has to do not only with the characteristics of the original material, but also with its processing and the final quality of the end-use products [8].

In 2009, Chattopadhyay et al. Studied the thermal and flame retardancy stability of polyurethane films based on HMDI and MDI [7].

In 2009, Giudice et al. formulated various technologies for coating paints based on expanded polystyrene [8].

In 2013, Benítez and Vélez obtained an anticorrosive coating from recycled expanded polystyrene using limonene with the main solvent [9].

In 2010, Zhang et al synthesized and characterized yellow water-borne polyurethane using a diol colorant as extender, They found that this material changed the optical properties of polydiacetylene; for example, the PUDA undergoes a color change under elastomeric strain (mechanochromism) [10].

In 2011, Shikata et al. studied Polystyrene solutions in cyclic monoterpenes present in the essential oils of trees, in order to develop an ecological reducing agent of expanded polystyrene [10].

In 2014, Jing Yang and colleagues studied polyurethanes to combat fuel attack and marine bio-corrosion [11].

This paper deals with the preparation of organic solvent based paints, using polyurethane polymers, expanded polystyrene

known commercially in Colombia as ICOPOR and light protective additives used in the polystyrene industry. It is anticipated that the paint to be synthesized will have physical and chemical properties comparable to commercial paints, besides having a stable thermal behavior. Finally, it is estimated that the film has favorable anticorrosive properties due to the hydrophobic nature of the expanded polystyrene material.

EXPERIMENTAL METHODOLOGY

MATERIALS

The following materials were used for the base preparation of the polyurethane paint: Polyol 287, Titanium Dioxide, Lomon 966, BYK 108 Dispersant, 12% Cobalt Octoate, 24% Zirconium Octoate, 10% Calcium Octoate, Xylene, Inprosolve, Polurene M 75, Butylglycol Acetate and Tinuvin®.

PREPARING THE PAINT

For the preparation of the modified polyurethane suspension, the following process was performed: In a resistant vessel, 2.5 kg of resin was homogenized for 10 minutes; with the aid of a mixing machine, it was shaken. Then, 0.5L solvent (Thinner polyurethane) was added, maintaining the shaking. Subsequently, 1.5 kg of titanium dioxide and 44 g of Dispersant were added under constant shaking. After homogenizing the mixture, 20g of 12% Cobalt Octoate, 20g of Zirconium Octoate 24%, 20g of Calcium Octoate and 44g of Dispersant (second addition) were added [5,12]. Maintaining the shaking for one hour, a solution of UV protective additive in polyurethane solvent was added until a concentration of 1000, 2000, 3000 and 5000ppm was obtained. Finally, from these mixtures five solutions, it was prepared five mix from one to five percent of polystyrene, giving rise to 25 modified formulations. At percentages above 1% of polystyrene, a segregation of colloidal suspension was observed; therefore, only formulations with up to 1% of polystyrene were tested.

PHYSICO-CHEMICAL CHARACTERIZATION

The characterization of the modified polyurethane films was performed using the following equipment and conditions:

Raman: excitation line of 785nm. Spectral region of 400 to 3200 cm^{-1}. 32 accumulations per spectrum. Approximate resolution of 1 cm-1, the spectra were taken on an EZRAMAN-N-785 portable spectrometer.

Infrared: Spectral region of 400 to 4000 cm^{-1}. 10 scans per spectrum. Approximate resolution of 4 cm^{-1}, the spectra were taken on a BRUKER OPTIC FTIR spectrometer.

Thermogravimetry: The thermograms were taken under the following analysis conditions: Heating ramp: 5°C/min, temperature range: 20 to 700°C, Nitrogen flow: 5L/min. The thermograms were recorded in a Universal V 4.5A TA Instruments brand thermobalance.

MECHANICAL PHYSICAL CHARACTERIZATION

The mechanical and physical performance tests were performed in the certified laboratory for coating films "Research, Innovation and Materials Development Center" (CIDEMAT) of the Universidad de Antioquia. The following tests were performed: Rheology viscosity (liquid paint), Gloss on painted plates (ASTM d523), Adhesion by pull off (ASTM d4541), Hardness pencil on painted plates (ASTM d3363), Impact with hammer BYK (ASTM d2794), Accelerated weathering chamber test, Saline chamber test. The above tests were applied to the polyurethane film with better physico-chemical properties, which was the formulation with 1000 ppm of the additive.

DISCUSSION OF THE RESULTS

Spectroscopic Characterization

Figure 1 shows the infrared spectra of the different synthesized formulations, of both commercial films and those with the additives tested. The high spectral similarity of the modified films can be appreciated with respect to the commercial film, specifically in the region from 800 cm^{-1} to 1800 cm^{-1} where the same spectral pattern is observed, with a slight difference in the intensities, which may be related to the concentration and crystallization state of the molecules and not to their molecular composition. Accordingly, it is inferred that it was possible to prepare a polyurethane film having molecular properties very similar to commercial films. Favourably, more intense bands are observed in the improved films spectra, which suggest that these films have more polymer units per area than the commercial benchmark film, which potentially can give greater protection to metal surfaces.

Because the proposed formulation included the addition of an ultraviolet light shield used in the polypropylene industry, ultraviolet light exposure tests were performed. The light exposure experiment was monitored with Raman spectroscopy for 30 consecutive days, and the spectra of greater variation were recorded in Figure 2. From the Raman spectral analysis, it is inferred that a polyurethane film with molecular properties very similar to the commercial films could be prepared, confirming the result of the infrared spectroscopy. At 15 days of light exposure, in the commercial and without additive films a widening of the characteristic bands was observed, which indicates a possible decomposition of the films. In the films doped with the UV additive, the widening was not observed, inferring that the tested additive offers UV protection to the PU films. In general terms from the second week of UV-exposure, PU films suffered damage by exposition to ultraviolet radiation. Consistently, a longer duration of whiteness was observed in the films with the protective additive.

Analysis of thermogravimetric (TGA) results

In addition to having an acceptable physical-mechanical behavior, the paint films must be stable against heating, which

means no decomposition or release of residual material by exposure to heat, for physical or chemical decomposition. Consequently, the different films were exposed to a heating in a temperature range from 20 to 700ºC. In this process characteristic losses of polyurethane films were observed in comparison to the commercial ones [8]. Sample one and two showed higher thermal stability of the commercial film, considering that at 350ºC, the temperature at which the first notable mass loss occurs, the film 1, 2 and without additive lost about 12% of its mass, while the commercial film 20%. Sample three and four showed higher mass loss. Taking into account the previous result, the most stable formulation or *UV*-doped film is that with a maximum amount of additive below 1000ppm. The films with higher concentration of additive presented greater loss at temperatures below 100ºC, which may be associated with an excess of non-retained additive (see figure 3).

Additionally, all PU films showed characteristic endothermic phase changes, except samples 3 and 4, which showed greater transformation and wider peaks, indicating low purity of the mixture and less uniformity, since the endothermic peaks showed a greater amplitude. Consequently, these variations may be associated with excess additive in formulations with a concentration greater than 1000ppm. With respect to polystyrene, no appreciable mass losses was observed (see figure 4). Finally, the results to the light exposure and TGA showed that the best formulation with the additive is that at a concentration of 1000ppm of *UV* protector and 1% of polystyrene.

Results of the performance tests

The performance tests were carried out on paint films with better physicochemical indicators, which were the formulation with up to 1000 ppm of the UV additive and that with 1% of polystyrene.

In accelerated weather chamber

With respect to this test, the film did not exhibit blistering or oxidation. All samples had a change of color perceptible to the naked eye with a whiter hue after 500 hours of UV. According to ASTM D523:14 used to measure gloss, when the gloss value at 60° is between 10-70 units, this measure is used. When the gloss value at 60° is more than 70 the value of the angle of 20° is normally taken and when the value is less than 10 the angle of 85°. This is why all values are taken at different angles. For all samples the gloss variations at an angle of 20° are relatively high after exposure to 500 hours of UV.

1.1.1. Viscosity by rheology

The results indicate that the paint has a behavior of a non-Newtonian fluid in the region of 0.001 to 1000 s -1, which is characteristic of a polyurethane-type paint. The system presented a pseudoplastic behavior where the viscosity is not constant in a shear rate range.

In spite of this, it can be considered that a painting at rest has a Shear rate of 1-10 s^{-1} which would be equivalent to a viscosity value of 13-30 Pa.s and a paint with brush application would have a Shear rate of 700s^{-1} which would be equivalent to a viscosity of 2.29 Pa.s.

Initial gloss before light exposure

The Gloss measurement was carried out with BYK equipment calibrated according to ASTM D523.

The gloss measurements were taken on four plates, two of them with base substrate in galvanized steel and two of them with bare substrate base steel. The results are shown in Table 1. The gloss values for the galvanized plates presented greater variation than the gloss values for the plates on a substrate of bare carbon steel. This result suggests that paint will perform better on carbon steel surfaces.

Table 1. Gloss values for two Galvanized samples and two samples of AC.

Galvanized simple				
Angle	**Gloss**			
20	61.6	60.6	61.7	61.3
60	92.1	91.3	92	91.8
85	92.8	90.3	92	91.7
Bare steel sample				
20	39.7	46.9	51.7	46.1
60	82.5	86.5	86.7	85.2
85	81.4	82.6	84.1	82.7

Pull-Off Adhesion analysis

The adhesion determination test of ASTM standard D4541: "Standard Test Method for Pull-Off Strength of Coatings Using Portable Adhesion Testers" is performed by attaching the dolly of the Pull Off equipment to the coating. A thin layer of adhesive is deposited in the center and allowed to cure at room temperature for 30 minutes. All samples follow the same procedure. Figure 5 and table 2 show the adhesion values in Psi. From the results of adhesion, it is inferred that the paint applied on galvanized substrate does not have good adhesion, while the paint applied on bare carbon steel does. Most of the faults were adhesive. Highlighting the effect of polystyrene, the film with 1% polystyrene showed greater adhesion than others one.

Table 2. Adhesion values for five samples on Galvanized and bare steel surfaces.

Sample	Value (Psi)				
	1	2	Commercial	3	No additive
Galvanized steel	250	200	300	100	100
	Adhesive	Adhesive	Adhesive	Adhesive	Adhesive
Bare steel	1100	1300	500	1100	1000
	Adhesive	Adhesive	Adhesive	Cohesiva	Cohesiva

Pencil hardness analysis

The hardness test is performed with a series of pencils with tips of different hardness, making a ¼" indentation at a 45° angle and determining the scratch resistance and resistance to penetration of the substrate. The hardness scale suggested by the standard is 6B-5B-4B-3B-2B-B-HB-F-H-2H-3H-4H-5H-6H (in the order of B-soft to H-hard). Figure 6 shows the results of the test. In summary, the 2H tip does not penetrate the paint on bare carbon steel, whereas on the paint on galvanized steel the H tip does penetrate. Both films are therefore classified as hard surfaces, typical of polyurethane films, by presenting greater crystallization, the film deposited on bare carbon steel.

Impact test analysis

The impact test was performed under ASTM D2794 with the aid of a BYK device, which performs a deformation on the plate and by means of the analysis of the failure of the coating with the failure point or the impact value of the same being determined in Pounds-inches. The values of the test are shown in Table 3. It is important to note that the standard suggests that the paint be applied on a steel panel that is 0.63 mm thick and the paints were applied on sheets of 3 mm, which will not undergo the same deformation as the standard sheet. In summary, the film on galvanized steel had an impact resistance of 2 Lb-in, while the sample on carbon steel showed greater impact resistance with 18 Lb-in. Therefore, we can say that the film has greater strength and adhesion on bare carbon steel.

Table 3. Impact test values

Sample	Impact value	Analyzed side	Ø stamp
	(lb-in)		(in)
Galvanised steel	2	Intrusión	0.623
Bare carbon steel	18	Intrusión	0.623

Exposure in salt spray chamber

The paint sample applied on galvanized steel substrate showed no blistering or oxidation after 500 hours in the salt spray chamber. However, the film on bare steel substrate showed the initiation of blistering in the area near the edges of the dielectric tape at 326 hours of exposure and from there it extended towards the center increasing in degree (up to 2MD) after 500 hours in the salt spray chamber. Surprisingly, the film with 1% polystyrene showed no signs of corrosion on both surfaces, which may be associated with the adhesion and hydrophobicity offered by polystyrene.

CONCLUSIONS

By means of the proposed methodology, it was possible to obtain a stable formulation using radiation protection compounds and traces of polystyrene, which is expected to prolong the preservation of the polyurethane film and protect any metallic surface. The physicochemical results showed that it was possible to obtain a polyurethane paint formulation of commercial-like composition. The thermal analysis showed that the films are stable and release little material at temperatures up to 400°C. The mechanical physical performance tests showed that the film of the proposed formulation meets the standard values established by the different international technical standards of the American Section of the International Association for Testing Materials (ASTM), surpassing the commercial films in the performance values in resistance to weather and saline environments.

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