Screen printing of UV curable polyurethane acrylate binder prepared with different pigment concentrations on synthetic leather and gloss and hardness properties of printed films

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Abstract. In this paper, UV curing technology and screen printing method were firstly together applied on synthetic leather, in order to determine the gloss and hardness values of screen printed UV curable polyurethane acrylate binder films prepared with different pigment concentrations. UV curable water-borne pigmented formulations were prepared with different pigment concentration (3%, 5% and 7%) and two types of photoinitiators (Omnirad® 500 and Omnirad® 819 DW). The curing process were conducted under different combinations of lamps (Ga, Hg, GaHg and GaGaHg) at three power levels. Pendulum hardness and gloss values of printed films were investigated. In gloss measurements, higher gloss values were obtained at the pigment concentration of 3% at all lamp combinations. Moreover, the highest gloss value (20.96) of the sample printed with 3% pigment concentration was obtained at GaHg lamp combination at 679 mJ/cm² energy density. The higher hardness values were obtained at a pigment concentration of 3% at all lamp combinations. The highest hardness value (9.8) of the pigmented polymeric films with 3% pigment concentration was obtained at GaGaHg lamp combination at 966 and 1663 mJ/cm² energy densities. The results show that high gloss and hardness values can be achieved at lower pigment concentration of 3%. Considering energy efficiency, curing under the GaHg lamp combination at an energy intensity of 679 mJ/cm² can be recommended for synthetic leather samples, which are printed with low pigment concentration (3%).

Keywords— Pigment concentration, polyurethane acrylate binder, screen printing, synthetic leather, UV curing.

1. Introduction

Pigment printing has attracted interest and the materials in the printing paste, such as pigments, binders, thickeners and etc., have been studied since mid-1940’s. According to a research conducted around mid-1980s, it has been presumed that more than half of the textile printed products in the world are produced by pigment printing. Pigment printing offers some advantages such as simplicity, removal of inexpensive wet post-processing, application to all types of fibers, printing styles and printing methods, and a wide choice of pigments in terms of color and light fastness preferences [1]. Conventional thermal curing techniques are generally used to bond the pigments to the textile surface. After printing, the product is dried and then subjected to a short-time fixing process with dry air at high temperature. At the end of fixing, the binder used polymerizes to form a film layer and allows the pigments to be held on the fiber [2,3]. UV curing technology is used to cure inks, coatings, adhesives and other UV-sensitive
The major advantages of UV cured coatings can be listed as, low cost and energy requirements, very fast cross-linking, application at room temperature, and the absence of volatile organic compounds which is harmful to the environment or health. UV curable formulations consist of oligomers, diluent monomers and photoinitiators. The main function of the photoinitiators is to initiate polymerization by forming a reactive group by absorbing the energy of the photons coming from the radiation during curing. All photochemical reactions are based on the activation of certain energy of excited molecules in the structure. Many types of photoinitiators contain at least one aromatic ring in which the carbonyl (C=O) group is present. For this reason, they strongly absorb UV rays. Molecules which are called as free radicals are stimulated by absorption of light energy by the photoinitiator and polymerization reaction occurs [3]. Almost all UV lamps used in UV curing units are based on mercury tubes. The standard mercury lamp is used in approximately 80% of the existing applications on the market. In a coating system, pigments or light stabilizers may absorb UV radiation and thus they can reduce the amount of free radicals produced by a photoinitiator. The main spectral output of the mercury lamp is below 300 nm and at 365 nm. In clearcoat applications, this spectrum can be used well with photoinitiator absorption. However longer wavelength absorption can be obtained with a gallium addition. Then intense output is added in the wavelength range of 400–450 nm. These lamp systems are suitable for pigmented coating applications which requires high UV intensity sources during polymerization reaction. In UV curing technology, one of the important factors for UV curing is the applied energy density at the coating surface, and the unit for the energy density is mJ/cm² [4].

Augusto et al. investigated changes in hardness, gloss and color values of water-borne clear and pigmented printing inks cured at different UV radiation levels. Pigmented formulations were prepared by using carbon black and organic pigments of low opacity and applied to the glass plates as a film of about 7.0 μm ± 1.3 μm by means of a film applicator. Coated films were cured in a device with a conveyor belt, under medium pressure mercury lamp and the effect of each pigment under UV light was examined. According to the results of the experiments, the average König hardness values of the clear polymeric films were much higher than those of the cured pigmented films. The pigments in the formulations led to the less absorption of UV light by the photoinitiators and this resulted in reduction of the curing level. Hardness values of the films obtained with formulations prepared with red and yellow pigments were lower than those obtained from blue and black pigmented formulations. Consequently, it was stated that the chemical structure of the pigments affected UV light absorption and the degree of curing could be changed. The color and gloss values in all formulations varied according to the applied energy density during curing. It was observed that films exposed to higher energy density during curing lost their gloss and exhibited yellowing due to deterioration on the surface [5].

Synthetic leathers have wide range of area of use – e.g., shoes, upholstery, automotive, leathercraft, and handbags, which features the patterns and the coloration methods. Although UV curable inks are applied with digital printing technology onto the synthetic leathers, the production speed is lower than that of conventional technologies, such as roller printing or screen printing. Particularly in coloration of shoes and upholstery products, conventional technologies are still in use. However, the printing pastes include solvent based binder and they are thermal curable [6,7]. Hence, in the current study, UV curing technology and screen printing method were firstly together applied on the synthetic leather, in order to determine gloss and hardness values of screen printed UV curable polyurethane acrylate binder films prepared with different pigment concentrations.

2. Experimental

2.1. Materials

Polyurethane (PU) based synthetic leather samples (Flokser Tekstil, Turkey) with a fabric weight of 545 g/m², were used as they are supplied. In the preparation of water-borne UV curable clear and pigmented formulations, a flexible, water-borne, aliphatic PU acrylate binder (Laromer® UA 9059, BASF, Germany) was used. Bisacyl phosphine (Omnirad® 819 DW, BASF, Germany) effective for deep curing and α-hydroxyketone (Omnirad® 500, BASF, Germany) effective for surface curing [4] were used as
the photoinitiators. Wetting agent (Exosel 54, Acar Kimya, Turkey), defoamer (Foamaster® 8034, BASF, Germany), anionic acrylic copolymer thickener (Orgaclear P 460, Organik Kimya, Turkey), deionized water and ammonia solution (NH$_4$OH, Kimetsan, Turkey) were also used in the formulation. Pigmented formulations were prepared using a red pigment (Irgazin® Red K 3840, CI Pigment Red 254, BASF, Germany).

3. Method

3.1. Preparation of printing pastes and printing
In this study, formulations were prepared with different pigment concentrations (%3, %5 and %7) separately and printed on synthetic leather samples by a flat screen printing machine. In the printing paste formulation, a flexible, water-borne, aliphatic PU acrylate resin (Laromer® UA 9059) as a binder and photoinitiators of bisacyl phosphine (Irgacure® 819 DW) and α-hydroxyketone (Irgacure® 500), pigment, wetting agent, defoamer, deionized water and ammonia solution (NH$_4$OH) were used. The pH and the viscosity of the formulations were arranged as 8.0-9.0 (with WTW Inolab pH 7110 pH meter) and 20,000-25,000 cP (at 20 rpm, with spindle 6 with a Brookfield DV-E viscometer), respectively. Water-borne UV curable printing paste formulation is given in Table 1.

| Table 1. Water-borne UV curable printing paste formulations. |
|---------------------------------------------------------------|
| Materials          | Quantity (%) |
| Deionized water   | 26           |
| Binder (Laromer® UA 9059) | 66           |
| (Irgacure® 500)   | 1.8          |
| (Irgacure® 819 DW) | 1.8          |
| (Irgazin® Red K 3840) | 3, 5 and 7  |
| Thickener         | 2.63         |
| Wetting agent     | 0.49         |
| Defoamer          | 0.1          |
| Ammonia           | 0.33         |
| Deionized water   | 26           |
| Binder (Laromer® UA 9059) | 66           |

3.2. UV Curing
After printing, samples were cured at room temperature using a UV curing machine equipped with gallium and mercury (Ga/Hg) lamps and a conveyor belt with an adjustable speed. In this study, total applied energy amount was measured with a UV-Integrator Type D radiometer (Table 2). UV curing of printed samples was conducted at 3 power levels (60, 90 and 120 W/cm) at a belt speed of 10 m/min under different UV lamp combinations (Hg, Ga, GaHg, GaGaHg).

3.3. Hardness measurement
For hardness measurements, pigmented films were prepared with a film applicator (Byk Gardner) on glass plates with a thickness of 120 μm and cured in UV curing machine. After UV curing, König hardness values of pigmented polymeric films were evaluated with a Byk Pendulum Hardness Tester according to ASTM D4366 [8] and the hardness values were reported in seconds. The procedure of the hardness tester is based on the oscillation of a pendulum which is released on the surface. The oscillation depends on the surface hardness. The period of oscillation is 1.4 seconds. In the measurements, the total
period of oscillation is calculated as multiplying one oscillation period by the number of oscillations [9, 10].

Table 2. Water-borne UV curable printing paste formulations.

| Power levels (W/cm) | Irradiation sources and Applied energy (mJ/cm²) |
|---------------------|-----------------------------------------------|
|                     | 60    | 90    | 120   |
| Ga                  | 186   | Ga    | 287   | Ga    | 497   |
| Hg                  | 288   | Hg    | 439   | Hg    | 731   |
| GaHg                | 444   | GaHg  | 679   | GaHg  | 1166  |
| GaGaHg              | 630   | GaGaHg| 966   | GaGaHg| 1663  |

3.4. Gloss measurements
In principle, gloss is defined as the ratio of light intensity reflected from the surface of an object to light intensity coming onto the surface. Hence, gloss is expressed by the amount of light reflected from the surface. Smooth and very glossy surfaces reflect more light. Gloss properties of surfaces are measured by a glossmeter which measures the specular reflection from the surfaces. There are three different geometries of the glossmeters. The widespread application of these geometries are 20°, 60°, 85° degrees which are used for the measurements of high, semi and low gloss values respectively. In addition, depending on the industrial applications, there are two more specific measurement geometries of 45° and 75° [11]. The gloss measurements of printed synthetic leather samples were made according to ASTM D523 [12], “Standard Test Method for Specular Gloss” standard using a Rhopoint, Novo-GlossTM glossmeter at 60° geometry.

4. Results and Discussions
4.1. UV Curing process and pendulum hardness measurement
In the preparation of the water-borne printing paste formulations, three pigment concentration were selected as 3%, 5% and 7% in order to determine the effect of pigment amounts. The pigmented pastes were prepared with equal amounts of photoinitiator (Omnirad® 819 DW and Omnirad® 500). Pigmented films were applied with the film applicator on glass plates at a thickness of 120 µm and cured in UV curing machine. The hardness of the pigmented films was measured by pendulum hardness tester and the hardness values were reported in seconds. The hardness values of UV cured pigmented films are shown in Table III. Distribution of the hardness values of pigmented films was shown in Fig. 1.

The hardness of polymeric films is directly related to the degree of polymerization reaction during UV curing. As a result of polymerization reaction, higher crosslinking density generally increases film hardness and it provides better abrasion resistance properties [13].

According to König hardness values of pigmented films (Table III), the increase in pigment concentration from 3% to 7% results in a decrease of hardness values. This can be explained by a reduction of the UV light absorption of the photoinitiators on the film surface due to pigment presence in the pigmented formulations. Decrease in hardness is related to decrease in curing degree due to the insufficient amount of free radicals which produced by photoinitiators required for polymerization. The higher hardness values (minimum 7 - maximum 9.8) were obtained at a pigment concentration of 3% at all lamp combinations. The highest hardness value (9.8) of the pigmented polymeric films with 3% pigment concentration was obtained at GaGaHg lamp combination at 966 and 1663 mJ/cm² energy densities. According to the results, although GaGaHg combination yielded the highest hardness value at 3% pigment concentration, the use of GaHg combination is suggested for curing considering the energy efficiency. The results suggested that higher gloss and hardness values can be obtained at lower pigment concentration of 3% and curing under GaHg lamp combination at 679 mJ/cm² energy density.
Table 3. Hardness values of UV cured pigmented films (B: UV cured pigmented film, P: Pigment).

| Lamp sources | Applied energy (mJ/cm²) | B %3P | B %5P | B %7P |
|--------------|-------------------------|-------|-------|-------|
| Hg           | 186                     | 8.4   | 7     | 7     |
|              | 287                     | 8.4   | 8.4   | 8.4   |
|              | 497                     | 8.4   | 8.4   | 8.4   |
| Ga           | 288                     | 8.4   | 7     | 7     |
|              | 439                     | 8.4   | 7     | 7     |
|              | 731                     | 8.4   | 7     | 7     |
|              | 444                     | 8.4   | 7     | 8.4   |
| GaHg         | 679                     | 8.4   | 8.4   | 8.4   |
|              | 1166                    | 8.4   | 8.4   | 8.4   |
|              | 630                     | 8.4   | 7     | 7     |
| GaGaHg       | 966                     | 9.8   | 9.8   | 9.8   |
|              | 1663                    | 9.8   | 9.8   | 9.8   |

Figure 1. Distribution of pendulum hardness values of pigmented films prepared with different pigmented (3%, 5% and 7%) formulations (B: UV cured pigmented film, P: Pigment).

4.2. Gloss measurements
Gloss values of printed and UV cured synthetic leather samples were shown in Table IV. Distribution of the gloss values of printed and UV cured synthetic leather samples was shown in Fig. 2. According to gloss measurement results (Table IV), increasing the pigment concentration affected the gloss values adversely and lower values were obtained in every lamp combination at different power levels. The pigment volume concentration (PVC) is the ratio of the total volume of pigment to the total dried material (film) present in printing. PVC affects various properties such as gloss, washability, strength, reflection and rheological properties. If there is enough amount of binder available in formulation, it completely encloses the pigment at a given pigment volume concentration and fills the gaps between the particles [14]. In this case the gloss of the surface is high because there is no light scattering in this concentration. However, as the pigment concentration increases, the pigment particles begin to protrude out of the binder surface, distributing the light falling on the surface and preventing the true reflection. For this reason, as the pigment concentration increases, the gloss decreases [15]. The higher gloss values (minimum 14.68 - maximum 20.96) were obtained at the pigment concentration of 3% at all lamp
combinations. Moreover, the highest gloss value of the sample printed with 3% pigment concentration was obtained at GaHg lamp combination at 679 mJ/cm$^2$ energy density.

Table 4. Gloss test results of printed and UV cured synthetic leather samples (A: printed synthetic leather sample, P: Pigment).

| Lamp sources | Applied energy (mJ/cm$^2$) | B %3P | B %5P | B %7P |
|--------------|----------------------------|-------|-------|-------|
| Hg           | 186                        | 8.4   | 7     | 7     |
|              | 287                        | 8.4   | 8.4   | 8.4   |
|              | 497                        | 8.4   | 8.4   | 8.4   |
|              | 288                        | 8.4   | 7     | 7     |
| Ga           | 439                        | 8.4   | 7     | 7     |
|              | 731                        | 8.4   | 7     | 7     |
|              | 444                        | 8.4   | 7     | 8.4   |
| GaHg         | 679                        | 8.4   | 8.4   | 8.4   |
|              | 1166                       | 8.4   | 8.4   | 8.4   |
|              | 630                        | 8.4   | 7     | 7.78  |
| GaGaHg       | 966                        | 9.8   | 9.8   | 9.8   |
|              | 1663                       | 9.8   | 9.8   | 9.8   |

Figure 2. Distribution of gloss values of printed and UV cured synthetic leather samples (A: printed synthetic leather sample, P: Pigment).

5. Conclusion
In the current study, water-borne UV curable formulations prepared with different pigment concentrations in order to determine the effects of pigment concentrations on gloss and hardness values of screen printed UV curable polyurethane acrylate binder films. UV curing technology and screen printing method were successfully applied together on the synthetic leather. According to the gloss measurement results, the increase in pigment concentration negatively affected the gloss values and low values were obtained in each lamp combination at different power levels. As the pigment concentration increases, the pigment particles begin to protrude from the surface and cause the light falling on the surface to disperse. For this reason, the actual reflection from the surface was inhibited and therefore low gloss values were obtained. High gloss values (minimum 14.68 - maximum 20.96) were obtained at a pigment concentration of 3% in all lamp combinations. Furthermore, the highest gloss value of the sample printed with a pigment concentration of 3% was obtained at an energy density of 679 mJ/cm$^2$ in a GaHg lamp combination.
When the results of the König hardness measurement of the pigmented films were evaluated, it was observed that the hardness values decreased by increasing the pigment concentration from 3% to 7%. These results are explained by the fact that in pigmented formulations the absorption of UV radiation in the film surface via photoinitiators is reduced by the pigments. Due to the reduced UV absorption, the hardness values decreased because of the insufficient amount of free radicals generated by the photoinitiators required for the polymerization. The better hardness values (minimum 7 - maximum 9.8) were obtained at a pigment concentration of 3% in all lamp combinations. The highest hardness value (9.8) of pigmented polymeric films with a pigment concentration of 3% was obtained at 966 and 1663 C energy densities in the GaGaHg lamp combination. According to the results, although the GaGaHg combination gives the highest hardness value at the 3% pigment concentration, the use of the GaHg combination for energy efficiency improvement is recommended.

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