

GLOSS AND HARDNESS EVALUATION OF WATER-BASED UV CURABLE POLYURETHANE ACRYLATE FILM USED IN TEXTILE PRINTING

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Abstract: In the current study, it is aimed to evaluate the hardness and gloss properties of water-based UV curable polyurethane (PU) acrylate films by using two types of photoinitiators at different ratios. For this purpose, UV curable water-based unpigmented and pigmented formulations were prepared. Formulations were applied on glass plates and UV cured under gallium and mercury (Ga/Hg) lamps at three different power levels, i.e., 60, 90 and 120 W/cm. After UV curing process, gloss and hardness values of polymeric films were measured. The highest film hardness values implying the highest curing level was obtained with the formulation A1, including only Omnirad® 819 DW (former Irgacure® 819 DW) which is effective in deep curing, and formulation A3 including Omnirad® 819 DW and Omnirad® 500 (former Irgacure® 500) effective in surface and deep curing at 2:1 ratio, respectively. Among these two formulations, the highest gloss value was obtained with the formulation A3. GaHg lamp combination provided the highest gloss values while highest film hardness values were obtained with GaHg and GaGaHg lamp combinations. Compared to clear films, pigmented films rendered higher gloss values which was more prominent in single lamp (Ga, Hg) cured films. Results showed that photoinitiators (Omnirad® 819 DW and Omnirad® 500) provided better hardness and gloss values at 1:1, 1:2 and 2:1 ratios. Gloss values increased due to the increase in film hardness. The increase in the total applied energy resulted in an increase in the film hardness values of all clear and pigmented formulations. In terms of film hardness and gloss values, films prepared with Omnirad® 819 DW and Omnirad® 500 at 1:1 ratio and cured under GaHg lamp combination provided better results.

Keywords: Water-based, polyurethane acrylate, photoinitiator, UV curing, gloss, hardness.

1 INTRODUCTION

UV curing technology is a fast, an easy to apply and an environmentally friendly method compared to conventional thermal curing, which can be applied in pigment printing [1, 2]. In this technology, different UV lamps may be used together due to the different spectrum of the lamps. The mercury (Hg) lamp is found sufficient for unpigmented formulations with spectral output at wavelengths <300 and 365 nm. In the case of pigmented formulations, however, the intensity of the UV sources is required to be increased to 400-450 nm range. This range can be obtained by adding gallium (Ga) to the lamp, which then called Ga lamp [3].

The UV curing mechanism is explained by the photopolymerization reaction of the binder. The photoinitiators absorb the energy of photons generated by irradiation and initiate the polymerization reaction by forming reactive groups during UV curing [2, 4]. These reactive groups lead to the cross linking of the binder which then results in film formation on the surface of the textile material. For the polymerization process of acrylic and styrene systems, different types of photoinitiators, possessing good chemical,

optical and mechanical properties, have been developed. It has been reported that UV curable formulations should consist of at least 0.3% photoinitiator and at least 10% binder [1]. However, different photoinitiator types and concentrations were investigated in some researches. In a study of Jancovicova et al., polymeric films including 2,2-dimethyl-2-hydroxyacetophenone (Darocure 1173) as photoinitiator were cured under medium pressured mercury lamp. The FTIR analyses were conducted to examine the polymerization degree of cured films. Results indicated that, photoinitiator concentration, applied energy at curing and film thickness have significant effect on curing mechanism of polymeric films [4].

Macarie et al. reported the color values and mechanical properties of the UV curable acrylic coatings which were prepared with photoinitiators p-methoxybenzoyldiphenylphosphine oxide (MBDPPO) and 2,2-dimethoxy-2 phenylacetophenone (Irgacure 651). The photoinitiators were used at 5:1 ratio versus monomer (Bisphenol-A epoxydiacrylate) amount. Results showed that pendulum hardness values and appearance properties such as color and gloss of cured films

were determined by the amount and content of pigment. Furthermore, appearance of the cured films was also affected by the particle size distribution of the pigment in the coating formulation. Pigments included in the formulations decreased the photoinitiator efficiency and thus the polymerization degree by absorbing UV light during curing [5].

Moreover, UV radiation doses may be changed to control film hardness and gloss for the evaluation of the polymerization level of the film [6, 7].

Pigment printing is widely applied due to its simplicity and cost effectiveness. Moreover, since the pigments have no affinity for the fibers, they are fixed on to the fibers with binders. However, in most of the pigment printing, the printing pastes include crosslinking agents, which are activated thermally. Hence, the fixation occurs at higher temperatures and requires longer fixation duration compared to UV curing systems [8].

In the current study, we aimed to evaluate the gloss and hardness values of UV cured clear and pigmented polyurethane acrylate films by the use of two different photoinitiators (*Omnirad® 819 DW* and *Omnirad® 500*) at different ratios.

2 EXPERIMENTAL

2.1 Materials

In the preparation of water-based UV curable clear and pigmented formulations, a flexible, water-based, aliphatic PU acrylate binder (Laromer® UA 9059) was used. Bisacyl phosphine (*Omnirad® 819 DW*) effective for deep curing and α -hydroxyketone (*Omnirad® 500*) effective for surface curing [9] were used as the photoinitiators. Wetting agent (Exosel 54, Acar Kimya, Turkey), defoamer (Foamaster® 8034, BASF), anionic acrylic copolymer thickener (Orgaclear P 460, Organik Kimya, Turkey), deionized water and ammonia solution (NH₄OH) were also used in the formulation. To obtain pigmented film a red pigment (Irgazin® Red K 3840, BASF) was used in the formulation.

2.2 Method

Water-based UV curable formulations were prepared using different photoinitiator ratios (0:3) of *Omnirad® 500* and *Omnirad® 819 DW*. Films of 120 μ m thicknesses were obtained with a film applicator (Byk Gardner) on glass plates. The pH and the viscosity of the pigmented and clear formulations were adjusted to 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. The clear formulation recipe is given in Table 1. The photoinitiator ratios used in formulations A1-A7 are given in Table 2. Formulations A1 and A3 were also prepared with 3% pigment with respect to binder amount. To determine the photoinitiator effect on gloss and

hardness properties of pigmented films, the formulations were prepared according to the Table 3.

Films were cured in UV curing equipment (Raycon®, Turkey) with an adjustable belt speed (2-50 m/min), and equipped with *Ga* (380 V) and *Hg* (220 V) lamps. UV curing was performed at three *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*). Due to the default properties of the UV lamps, which are mounted on the UV curing equipment, the power levels can be adjusted between 60 W/cm - 120 W/cm individually. Hence, the energy output of the UV lamps depends on the adjusted power. However, depending on the belt speed, the total applied energy amount can vary. Thus, the total applied energy was measured with a UV-Integrator Type D radiometer.

The chemical changes in the cured films were characterized by FTIR spectroscopy (PerkinElmer FTIR C99089). The gloss measurements of polymeric films were made according to ASTM D523, "Standard Test Method for Specular Gloss" standard using a Rhopoint, Novo-Gloss™ glossmeter at 60° geometry. After UV curing the König hardness of polymeric films were evaluated with a Byk Pendulum Hardness Tester.

Table 1 Clear formulation

Materials	Quantity [g]
Deionized water	26
Binder (Laromer® UA 9059)	66
Photoinitiators	3.6
Thickener (Orgaclear® P 460)	2.63
Wetting agent	0.49
Defoamer	0.1
Ammonia	0.33
Total	100

Table 2 Photoinitiator ratios used in the clear pastes

Formulations	Omnirad® 500	Omnirad® 819 DW
A1	-	3
A2	0.5	2.5
A3	1	2
A4	1.5	1.5
A5	2.0	1.0
A6	2.5	0.5
A7	3.0	-

Table 3 Photoinitiator ratios used in the pigmented pastes

Formulations	Omnirad® 500	Omnirad® 819 DW
X1	1	1
X2	1	2
X3	1	3
X4	1	4
X5	1	5
Y2	2	1
Y3	3	1
Y4	4	1
Y5	5	1

3 RESULTS AND DISCUSSION

3.1 Hardness measurements

The highest clear film hardness was obtained with the formulation A1, including only *Omnirad*® 819 DW which is effective in deep curing, and formulation A3 including *Omnirad*® 819 DW and *Omnirad*® 500 effective in deep and surface curing at a ratio of 2:1 (Figure 1).

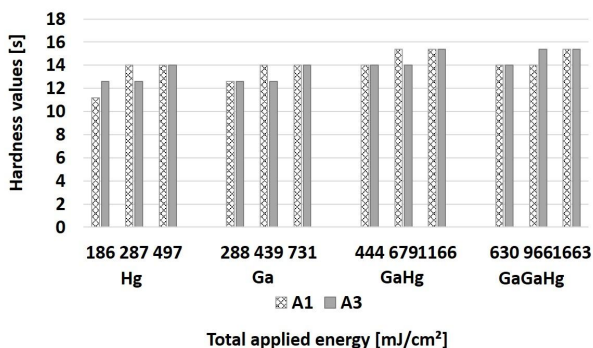


Figure 1 The effect of applied energy on hardness properties in clear formulations A1 and A3

In general, the film hardness values decreased with the decrease in the amount of *Omnirad*® 819 DW photoinitiator (effective in deep curing) in the formulation. The increase in the total applied energy resulted in an increase in the film hardness values of all clear formulations. Both *GaHg* and *GaGaHg* lamp combinations yielded higher film hardness values. Among the films cured under *GaHg* lamp combination at 120 W/cm power level, the difference between the highest hardness values (A1) and the lowest hardness value (A6) is 42.8%. Photographic images of clear films are given in Figure 2.

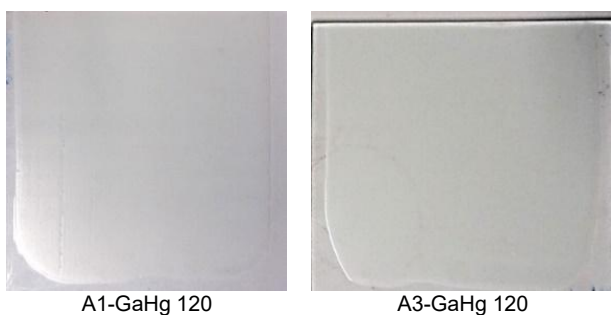


Figure 2 Photographic images of clear films prepared with A1 and A3 formulation cured under *GaHg* lamp combination at power level of 120 W/cm

The effect of applied energy on hardness values in pigmented formulations A1 and A3 is shown in Figure 3. Hardness results showed that pigmented films have low hardness values when compared with those of clear films (Figure 1). The highest hardness values were obtained in pigmented films which are

obtained after curing under both *GaHg* and *GaGaHg* lamp combinations. The polymerization degree of the films prepared with pigmented formulations decreases in comparison with that of clear formulations. Since, pigments absorb more UV light and hinder the formation of the free radicals, which provides the polymerization reaction of the binder, the polymerization degree decreases in pigmented films [10]. Photographic images of pigmented films are given in Figure 4.

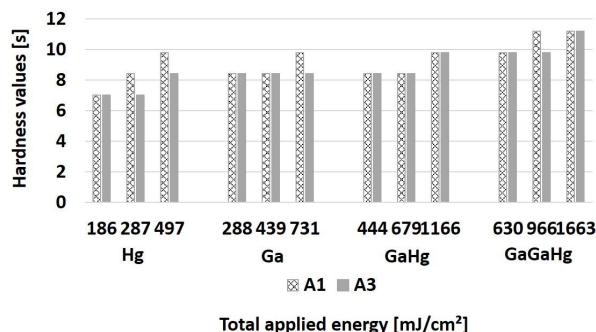


Figure 3 The effect of applied energy on hardness properties in pigmented formulations A1 and A3

To determine the effect of photoinitiator type on hardness properties of pigmented films prepared according to Table 3 were subjected to pendulum hardness test. Results showed that the highest hardness values were obtained in films prepared with X1 formulation including the same *Omnirad*® 819 DW and *Omnirad*® 500 ratios.

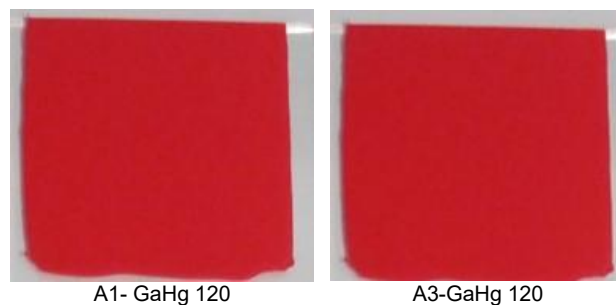


Figure 4 Photographic images of pigmented films prepared with A1 and A3 formulation cured under *GaHg* lamp combination at power level of 120 W/cm

The film hardness values decreased with the increase in the amount of *Omnirad*® 819 DW photoinitiator (effective in deep curing) in the formulation. The lowest hardness value was obtained with the formulation X5 including *Omnirad*® 500 and *Omnirad*® 819 at a ratio of 1:5 (Figure 5). This situation was also observed when the ratio of *Omnirad*® 819 kept constant and *Omnirad*® 500 was increased gradually. Hence, the film hardness values decreased with the increase only in the amount of *Omnirad*® 500 DW photoinitiator (effective in surface curing) in the formulation.

The lowest hardness value was obtained with the formulation Y4 including *Omnirad*® 500 and *Omnirad*® 819 at a ratio of 5:1 (Figure 6) The hardness values of the formulations X5 and Y4 were obtained the same value, which is 9.8 s under same lamp combination and total applied energy.

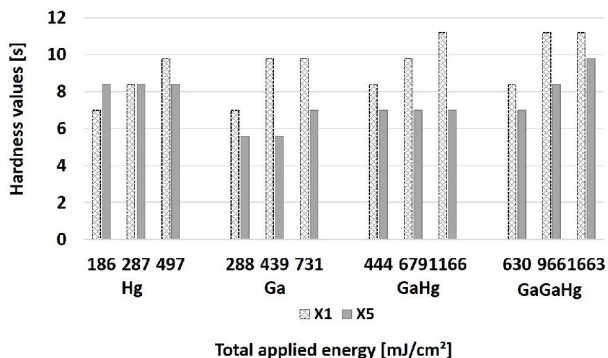


Figure 5 The effect of applied energy on hardness properties in pigmented formulations X1 and X5

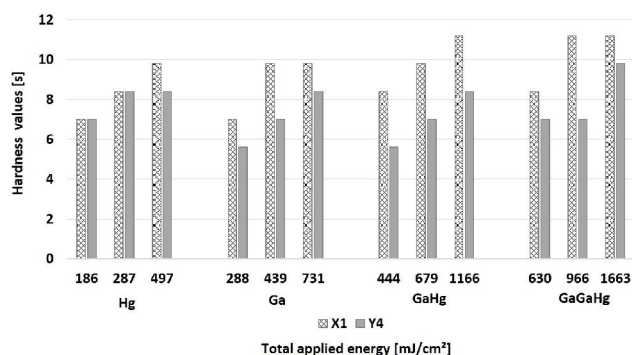


Figure 6 The effect of applied energy on hardness properties in pigmented formulations X1 and Y4

Results showed that photoinitiators should be used at the ratio of (1:1) due to the synergetic effect, instead of increasing the ratio of each photoinitiator alone. The more effective film hardness values were obtained in films prepared with X1 formulation cured under both *GaHg* and *GaGaHg* lamp combinations.

3.2 Gloss measurements

The highest gloss values were obtained in films prepared with A3 formulation cured under *GaHg* lamp combination (Figure 7). It can be suggested that there is a synergetic effect towards improvement of gloss when two photoinitiators are combined in the same formulation. In accordance, when the amount of photoinitiator *Omnirad*® 500 increases, the gloss values improved until a certain value. After this value, gloss values tend to decrease. The effect of the total energy applied in the curing process on the gloss values for both clear and pigmented films is shown in Figure 8 for A3 formulation. For clear films, the higher gloss values

were obtained for *GaHg* lamp combination but in pigmented films, the higher gloss values were obtained in films cured under *Ga* lamp. However, hardness results showed that curing with a single *Ga* lamp provided low film hardness, indicating a low degree of curing. It is concluded that in order to obtain sufficient film hardness and gloss values, *GaHg* lamp combination should be preferred in curing.

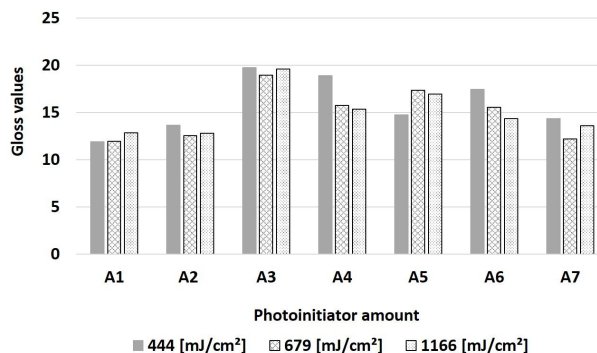


Figure 7 The effect of photoinitiator amount on gloss values of clear films cured under *GaHg* lamp combination

Gloss values of the pigmented films which were prepared according to the photoinitiator ratios given in Table 3, decreased with the increase of the *Omnirad*® 819 DW photoinitiator. The increase in the total applied energy for each lamp combination resulted in an increase in the gloss values of all pigmented formulations. The highest gloss values were obtained in films prepared with X2 formulation including *Omnirad*® 819 DW and *Omnirad*® 500 at a ratio of 2:1.

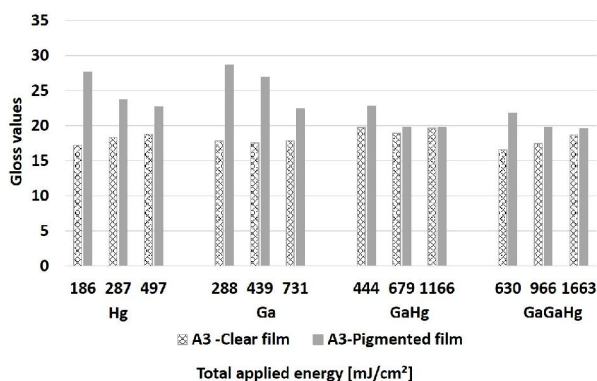


Figure 8 The effect of applied energy on gloss values of clear and pigmented films cured under different lamp combinations

The lowest gloss values were obtained with X5 formulation including *Omnirad*® 819 DW and *Omnirad*® 500 at a ratio of 5:1 (Table 3). Gloss values of X2 and X5 formulations are given in Figure 9.

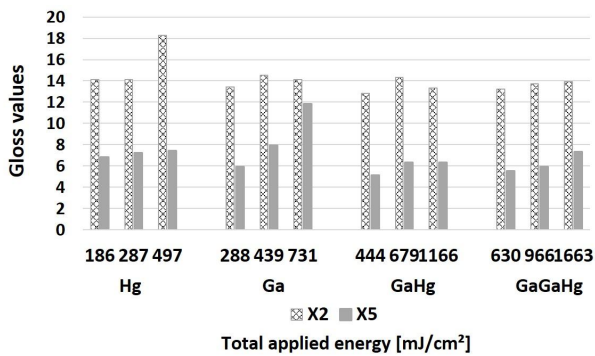


Figure 9 The effect of applied energy on gloss values in pigmented formulations X2 and X5

Moreover, the gloss measurements at all power levels were repeated 5 times. Hence, the *t* tests show that difference between X2 and X5 formulations in terms of gloss values are significant, since the calculated *t* values are higher than that of the correspondence value at *t* table (95% confidence, 8 degree of freedom) in all power levels excluding 60 and 90 W/cm at single Hg lamp. Figure 10 shows the calculated *t* values versus correspondence *t* value of the table X2 - X5.

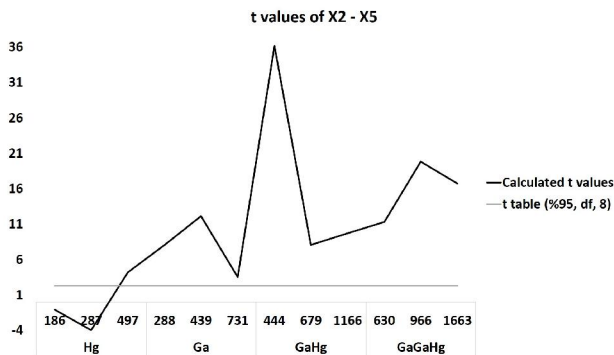


Figure 10 Calculated *t* values of X2 - X5 at all power levels and lamp combinations

The gloss values of the films increased with the increase in the amount of Omnirad® 500 photoinitiator. The highest gloss values were obtained in films prepared with Y4 formulation including Omnirad® 819 DW and Omnirad® 500 at a ratio of 1:4. This can be explained by the fact that surface curing effect of Omnirad® 500 photoinitiator provides high gloss value. At the same time films prepared with Y4 formulation has lowest hardness values. These results cause deterioration and opening of the film surface due to low strength after a certain period of time.

The lowest gloss values obtained with the films prepared with Y2 formulation which have high hardness values when compared with film prepared with Y4 formulation. In Figure 11, the *t* tests show that difference between Y2 and Y4 formulations in terms of gloss values are significant, since the calculated *t* values are higher than that

of the correspondence value at *t* table (95% confidence, 8 degree of freedom) at all power levels (60, 90, 120 W/cm).

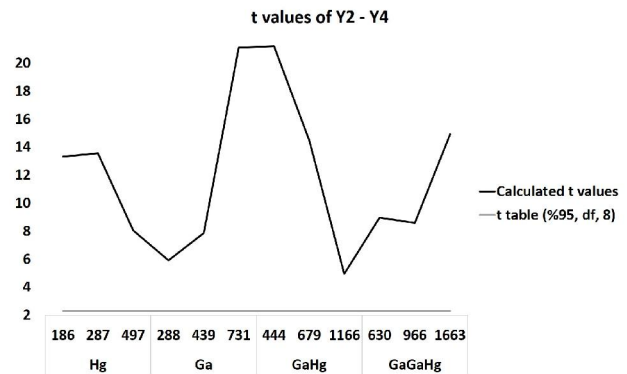


Figure 11 Calculated *t* values of Y2 - Y4 at all power levels and lamp combinations

Gloss values of X1, Y2 and Y4 formulations are given in Figure 12. In terms of film hardness and gloss values, films which are prepared with X1 formulation and cured under *GaHg* lamp combination, could be suggested.

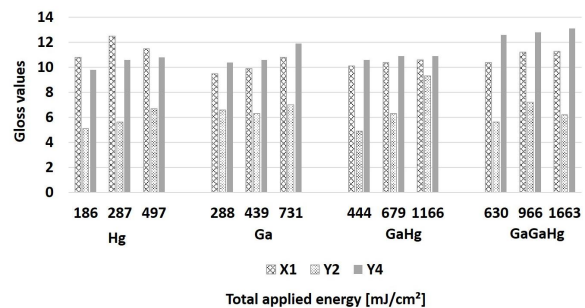


Figure 12 The effect of applied energy on gloss values in pigmented formulations X1, Y2 and Y4

3.3 FTIR spectroscopy

FTIR analysis of the clear films showed that there was a reduction and a disappearance of the twisting peak of $-CH_2=CH_2$ at 810 cm^{-1} wave number and bending peak at 1.410 cm^{-1} wave number, which suggested the development of the cure. Figures 13 and 14 show the FTIR spectrums of clear films prepared with A1 and A3 formulation and cured under *GaHg* lamp at different power levels (60, 90 and 120 W/cm), respectively.

Figures 15 to 17 show the FTIR spectrums of pigmented films prepared with X5, Y4 and X1 formulations and cured under *GaHg* lamp at different power levels (60, 90 and 120 W/cm). Although FTIR analysis of the clear films showed that there was an evidence for the development of the cure, this could not be observed in the pigmented formulations. This was due to the presence of the pigments, which prevented the observation of the expected scissor deformation peak at wave numbers 1538 cm^{-1} .

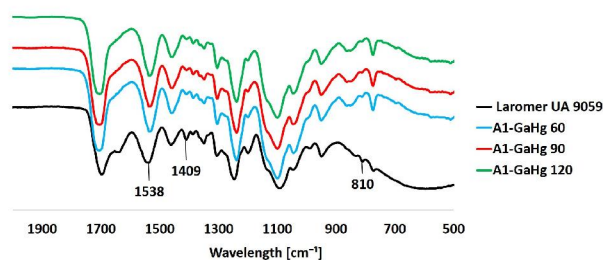


Figure 13 FTIR spectrum of clear film prepared with formulation A1

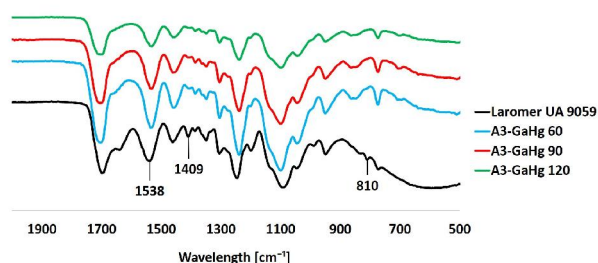


Figure 14 FTIR spectrum of clear film prepared with formulation A3

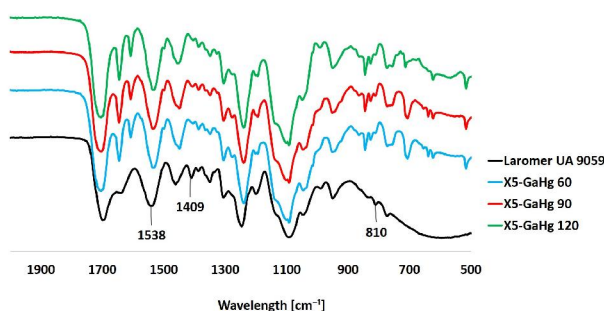


Figure 15 FTIR spectrum of pigmented film prepared with formulation X5

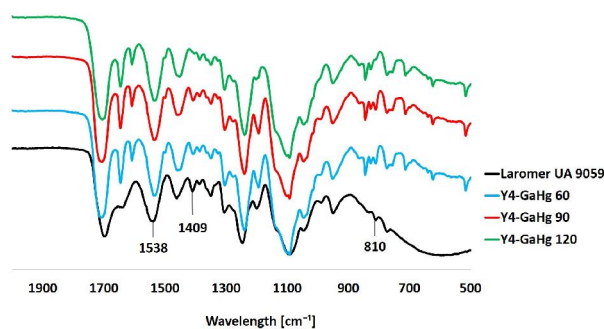


Figure 16 FTIR spectrum of pigmented film prepared with formulation Y4

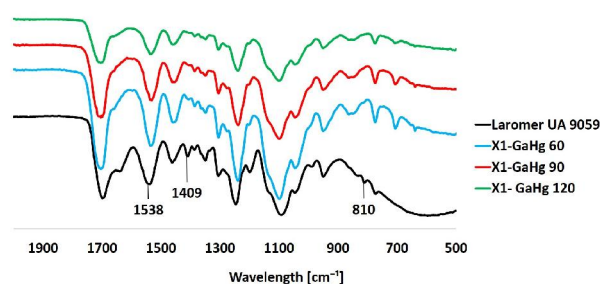


Figure 17 FTIR spectrum of pigmented film prepared with formulation X1

4 CONCLUSION

According to gloss measurement results, the higher gloss values were obtained with clear A3 formulation which includes *Omnirad*® 500 and *Omnirad*® 819 DW, photoinitiators at a ratio of 1:2, respectively. The best hardness values were obtained in films prepared with A1 formulation including only *Omnirad*® 819 DW, cured with GaHg lamp; however the gloss values of this formulation were the lowest among all formulations. Formulation A3 provided optimum gloss and hardness values. The hardness and gloss values of the films prepared with pigmented formulations showed that photoinitiators should be used in a ratio of (1:1) instead of increasing the amount of the photoinitiators individually. The higher film hardness values were obtained in films prepared with X1 formulation cured under both GaHg and GaGaHg lamp combinations. In terms of film hardness and gloss values, films prepared with the formulation X1 and cured under GaHg lamp combination at high power level (120 W/cm) can be suggested. Although the highest hardness values were obtained with the GaGaHg lamp combination, considering the energy efficiency and curing level, GaHg lamp combination could be recommended for curing.

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