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Research Article

Preparation and Application of Urethane Acrylate Coatings for Enhanching Mechanical Properties of Coagulated Surfaces

Koagüle Yüzeylerin Mekanik Özelliklerinin İyileştirilmesi için Üretan Akrilat Kaplamaların Hazırlanması ve Uygulaması

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Abstract

Radiation curing is the polymerization of a chemical system which is initiated by incident radiation. The curing, the transformation from a liquid into a non-tacky solid, is very fast and occurs in less than one second. There are two major reasons for the current rapid advance of UV-curing technology; one of them is energy and matter conservation and the other is environment pollution control. Diluents, particularly multifunctional acrylate monomers, are used to reduce viscosity to manageable levels and to provide crosslinking. In this work, the aim was to develop some formulations with urethane prepolymer to improve mechanical properties of coagulated polyurethane surfaces with desired properties. Aromatic (ARUA) and Aliphatic Urethane Acrylate (ALUA) Oligomer based formulations were prepared. Those formulations were applied on coagulated polyurethane surfaces and aluminium plates which is used for free films. Samples are cured with UV radiation with different conveyor speeds. As a second step, obtained ALUA and ARUA free films (films peeled off aluminium plates) and treated coagulated polyurethane surfaces were tested for their physical and mechanical properties.

Keywords: Coagulated polyurethane, Urethane acrylate, UV radiation

Öz

Işıma ile kürleme, kimyasal bir sistemin ani bir ışıma tarafından başlatılan polimerizasyonudur. UV radyasyonla bir sıvının yapışmayan bir katıya dönüşmesi olayı, bir saniyeden kısa bir sürede meydana gelir. UV kürleme teknolojisinin şu anki hızlı gelişiminin en önemli iki sebebinden biri enerji ve maddenin korunması, diğeri ise çevresel atık kontrolüdür. Viskoziteyi düşürüp kullanılabilir düzeylere indirmek ve çapraz bağlanmayı sağlamak için çok fonksiyonlu akrilat monomerler olan seyrelticiler kullanılır. Poliüretan koagüle zeminler, en çok suni deri üretiminde kullanılmaktadır. Çok fonksiyonlu sıvı akrilat monomerler ile viskoz oligomerlerden, çapraz bağlı polimer ağı elde etmenini en etkili ve kolay yöntemi fotopolimerizasyondur. Kürleme mekanizması ise malzemenin belirli dalga boyundaki UV ışığa duyarlı, kimyasal bileşenlerine dayanır. Bu çalışmada, suni deri uygulamasına yönelik, alifatik ve aromatik üretan akrilat oligomerlerden, UV ışınları ile, istenilen özelliklerde, polimerik kaplamalar elde edilmeye çalışılmıştır. Elde edeceğimiz polimerik filmin mekanik özelliklerini belirlemede oldukça etkin bir rol oynadığından farklı oranlarda değişik fonksiyonlu akrilat monomerleri ilavesi ile formülasyonlar hazırlanmıştır. Hazırlanan fomulasyonlar uygun fotobaşlatıcı ortamında kaplama yüzeyine uygulanarak, UV ile kürleştirilmiş, daha sonra da fiziksel ve mekanik özellikleri incelenmiştir.

Anahtar Kelimeler: Koagüle poliüretan, Üretan akrilat, UV ışıma

1. Introduction

Polyurethane resins are widely used in coating applications especially in production of coagulated polyurethane surfaces because of their high performances. Coagulated polyurethane surfaces are used as synthetic leather which is an important commodity that is widely used in shoes, luggage carriers, bags and as sheaths for couches etc. Urethane acrylate oligomers have been extensively investigated in the past two decades as photocurable coatings useful for protecting some material surfaces such as papers, woods and plastics (Chen et al. 2008, Jun Hua and Pu Hu 2000, Kim et al. 2006, Lee and Kim 2007). They are high molecular weight, reactive materials that can be photopolymerized (cured) using a free radical mechanism called ultraviolet (UV) radiation. Photoinitiated

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free radical polymerization of urethane acrylate oligomers require reactive multifunctional diluents that enhanche mechanical properties and an appropriate photoinitiator that starts photopolymerization (Endruweit et al. 2006, Wang and Hsieh 2007, Yu et al. 2001). UV-radiation curing has become a well accepted technology which has found a large variety of industrial applications because of its distinct advantages. Light-induced polymerization of multifunctional oligomers and monomers is indeed a powerful method to achieve a quasi-instantaneous transformation of a liquid resin into a solid polymer. The steady development of the UV-curing technology in the past 20 years has opened the way to an increasing number of end uses. The most important ones are to be found in the coating industry for enhancing final properties and surface protection of the product. This work will concern the preparation of aliphatic and aromatic urethane acrylate formulations which is applied on coagulated polyurethane surfaces and their polymerization by UV light. The aim is enhanching mechanical properties of coagulated surfaces. Therefore, physical and mechanical properties of the treated and untreated surfaces were investigated.

2. Material and Methods

2.1. Oligomers

All materials are used as obtained without further purification. Diacrylate functionalized Aliphatic Urethane Acrylate oligomer (ALUA) which was prepared by polyaddition reaction of the appropriate amount of polyol (polyetherol or polyesterdiol), a hydroxy-functionalized acrylate, and aliphatic diisocyanate by standard procedures (Kim et al. 1996). Diacrylate functionalized Aromatic Urethane Acrylate oligomer (ARUA) which was prepared by polyaddition reaction of the appropriate amount of polyol (polyetherol or polyesterdiol), a hydroxy-functionalized acrylate, and aromatic diisocyanate by standard procedures.

2.2. Monomers

Isodecyl acrylate (IDA) is a monofunctional acrylic monomer which can be polymerised by free radicals. It is used in UV cured coatings, inks and adhesives. The following key properties are offered by isodecyl acrylate to formulations: Excellent solvency, Low shrinkage, good adhesion, excellent water resistance, good flexibility.

Propoxylated Neophentyl Glycol Diacrylate (NPGDA) is a difunctional acrylic monomer. NPGDA is a very low viscosity oligoether acrylate which can be polymerised by free radicals. In particular it is used in UV cured coatings, inks and adhesives. The following key properties are offered by propoxylated NPGDA to formulations: Good solvency, good flexibility, good chemical resistance, excellent wetting properties. Propoxylated Glyceryl Triacrylate (GPTA) is a trifunctional acrylic monomer. GPTA monomer offers, good flexibility, fast curing, low viscosity, good solvency, good reactivity, good chemical resistance, excellent hardness. Trimethylolpropane triacrylate (TMPTA), which is a trifunctional acrylic monomer offers, low viscosity, low volatility liquid monomer, offers fast cure response, low volatility during free-radical polymerization

2.3. Other Chemicals and Reagents

Acryloxy Organo Polysiloxane is a linear acryloxyorgano-functional polysiloxane. Due to the acryloxy end groups, it can be used as a reactive component in suitable polymers. It provides; gloss, flexibility, hydrofobicity. 1-Hydroxy-

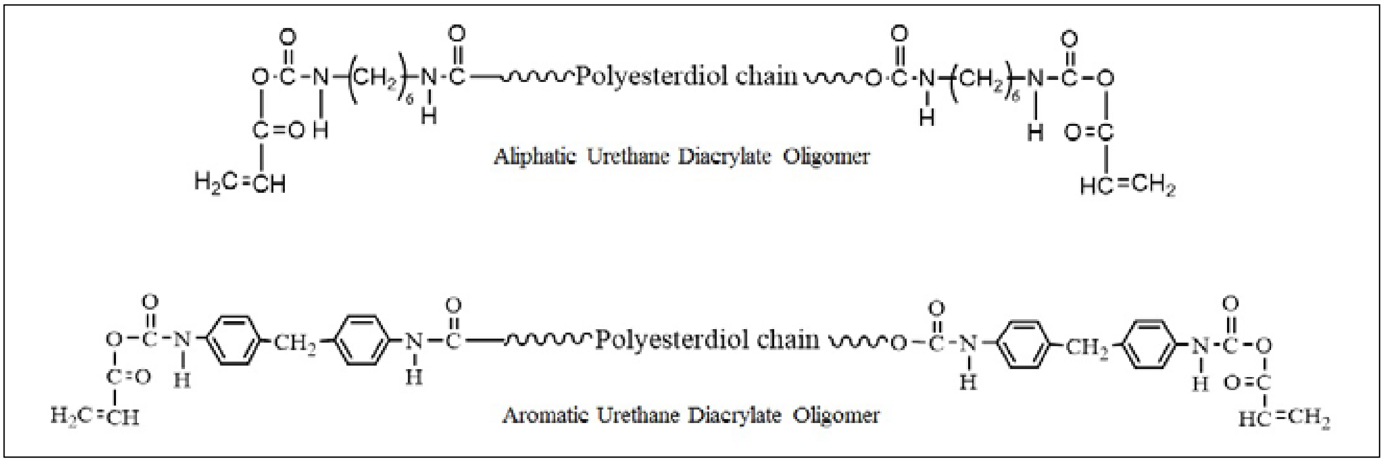


Figure 1. Oligomers.

cyclohexyl-phenyl-ketone (Irgacure 184) which is a alpha clevage type photoinitiator. It is white to off white solid photoinitiator that can be dissolved in liquid acrylic monomers.

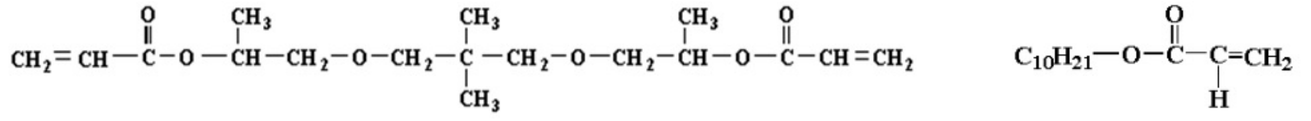
2.4. Equipments

A conveyor type UV curing machine (EMA) using UV lamps (254–313 nm,12 kW/m), donated with adjustable conveyor speeds was used for photoinitiated polymerization of formulations. UV curing machine is shown at Figure 4.

A König Pendulum Hardness (Gardner, BYK) tester was used to measure the film hardness of the UV-cured films. Tensile (uniaxially loading) tests for cured films were carried out and recorded with a horizontal tensile loading machine. Spectrophotometric analysis of UV cured treated and untreated coagulated polyurethane surfaces was performed with a Scinco (S-3100) instrument. The formulations were coated on aluminium plates and coagulated surfaces by a bar coater (Gardner BYK) (25μ).

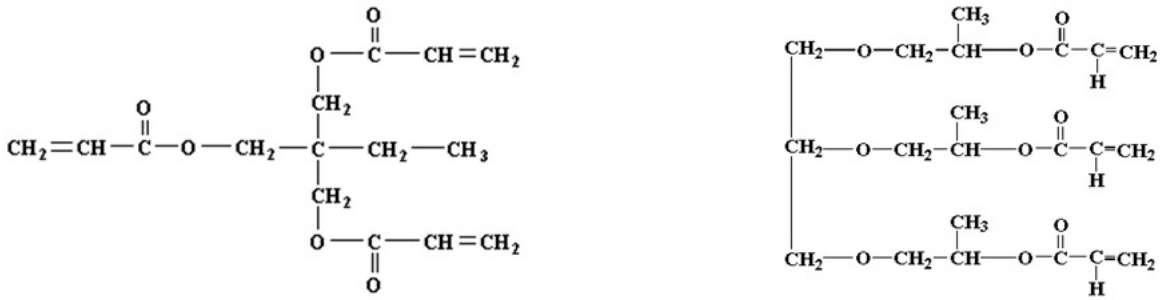
2.5. Preparation of Formulations

Two different formulations including urethane acrylate oligomers, reactive diluent monomers, additives and photoinitiator were developed. Aromatic urethane acrylate oligomer formulation was prepared. ARUA composition is shown at Table 1.



Propoxylated Neophentyl Glycol Diacrylate (NPGDA)

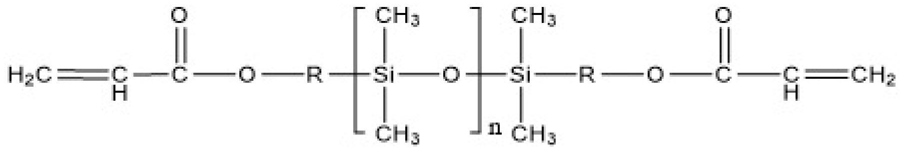
Isodecylacrylate (IDA)



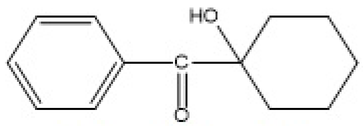
Trimethylolpropane triacrylate (TMPTA)

Propoxylated Glyceryl Triacrylate (GPTA)

Figure 2. Monomers.



Acryloxy organo polysiloxane



1-hydroxy-cyclohexyl-phenyl-ketone

Figure 3. Other chemicals and reagents.

Aliphatic urethane acrylate oligomer formulation was prepared; ALUA composition is given in Table 2.

2.6. Application

The formulated solutions were cast onto Aluminium (Al) plates (6 x 15 cm) to obtain free films and coagulated polyurethane surfaces (CPS) (6 x 15 cm) using a bar coater. 4 Al Plate and 4 CPS substrates were coated for each of the formulations (ALUA and ARUA). For photopolymerization via UV radiation, a conveyor type UV curing machine is used. Totally 16 samples are passed 8 times under the radiation source to ensure curing of the film. Samples are cured under UV light at different conveyor speeds of 0.1 m/min; 1,0 m/min; 2,0 m/min; 3,0 m/min.

2.7. Analysis

Following tests, Pendulum Hardness, gel content, solvent swelling ratio, water uptake ratio, surface reflectivity and tensile properties tests are performed to monitor physical and mechanical properties of samples. The pendulum is placed on the coating with the two balls 5 mm in diameter and moved 6° away from the position of rest. After releasing the 200 g pendulum the oscillations are recorded by a counter. The measure of damping is the number of oscillations or the time in seconds which elapses until the amplitude of the pendulum has dropped from 6° to 3°(Goldschmidt and Streitberger 2003). Pendulum hardness (PH) of the UV-cured film was measured to determine the film hardness and the UV dose intensity at which the film is properly cured (Azam Ali et al. 1996). The test device is shown in Figure 5.

The tests were applied while the cured film was still on the CPS surface and after cured film was peeled off Al plates. For analyzing the gel content a known weight of the free

Figure 4. EMA UV curing machine.

Table 1. Aromatic urethane acrylate formulation (ARUA).

Oligomer	Aromatic urethane diacrylate
Monofunctional acrylic monomer	Isodecyl acrylate
Difunctional acrylic monomer	Neophentyl glycol diacrylate
Trifunctional acrylate	Propoxylated glyceryl triacrylate
Polysiloxane	Acryloxy functional polysiloxane
Photoinitiator	1-Hydroxy-cyclohexyl-phenyl ketone

Table 2. Aliphatic urethane acrylate formulation (ALUA).

Oligomer	Aliphatic urethane diacrylate
Monofunctional acrylic monomer	Isodecyl acrylate
Trifunctional acrylate	Propoxylated glyceryl triacrylate
Trifunctional acrylate	Trimethylol propane triacrylate
Polysiloxane	Acryloxy functional polysiloxane
Photoinitiator	1-Hydroxy-cyclohexyl-phenyl-ketone

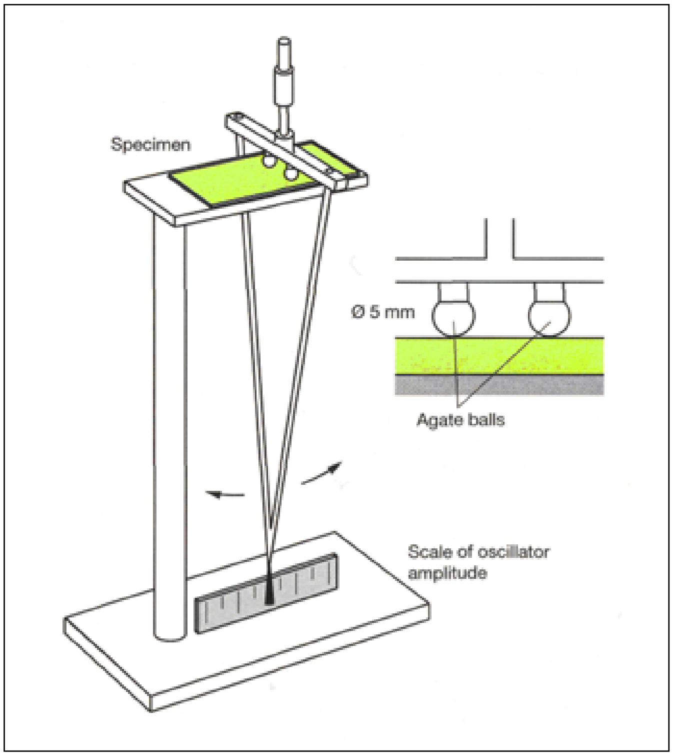


Figure 5. König pendulum hardness tester.

film; cured film peeled off the Al plate; was wrapped in a stainless-steel net that was put in a Soxhlet. Unreacted monomers were removed through extraction in hot benzene for 48 h in the Soxhlet. It would be difficult for benzene to remove large molecular compounds like polymers via the extraction process. The difference of weights of the cured film before and after the extraction determined the gel content (Ali et al. 1998, Khabir Uddin et al. 1996). As previously mentioned UV curing provides high conversions as a result high crosslink densities. At high crosslink densities solvent swelling can be used to determine extent of crosslinking. While crosslinked films do not dissolve in solvent, the solvent does dissolve in crosslinked film. As crosslinks get closer together, crosslinking density increases and the extent of swelling decreases (Wicks et al. 2007). The more a film is cured and crosslinked, the less ability it has to swell, because the swelling molecule, in that case, can hardly find enough functional group and space to swell the cured polymer through loose bonding or so (Khan et al. 2002). Thus, as the crosslinking density (curing) increases, the swelling ratio is expected to decrease. A known weight of each extracted free film sample was soaked in acetone for 24 h at 25 °C. The weight difference of the swollen film with that of the dry extracted film yields the swelling ratio (Khabir Uddin et al. 1996). Also water uptake is an important test for determining polymers water resistance. The extent of water uptake was determined by putting a drop of water on untreated and ARUA, ALUA treated CPS. The wet time period of the water drop on samples was 5 minutes. The results were obtained from increased weight of the material due to water absorption during the period the water drop was allowed to stay on the surface. The reflection of light varies depending on the smoothness of the surface so the illuminated environment is reproduced more or less efficiently. The reflection curve of a coating thus permits an objectively accurate description of the physical property of color without any subjective influences, as are bound to occur if the human eye perceives a color impression. The sensory impression complex resulting from light consists of the interactions of the light reflected in the surface (gloss) and the component penetrating and then scattered back diffusely (color). This reflectance R (λ) is measured with the aid of a spectrophotometer. To monitor gloss factor International Commission of Illumination (CIE) recommends some different geometries of measuring probe for coatings (Goldschmidt and Streitberger 2003). Illumination at 45° / measurement at 0° (45/0) and Illumination at 0° / measurement at 45° (0/45). In this study, Illumination at 0°/ measurement at 45° was studied with ALUA and ARUA treated CPS samples. Tensile properties are important to the performance of radiation cured coatings as they directly impact the performance of the cured film. Tensile is the greatest stress a coating can withstand prior to breaking (Wicks et al. 2007). Modulus is a measure of the stress required to elongate the film a given distance and elongation at break is the distance a film will stretch before breaking. Tensile properties are very important in choosing a particular polymer for a specific application. Sometimes, a polymer of high tensile strength with moderate or low elongation, or vice versa, is desirable.

Thus, different formulations need to be developed while considering all these factors. As explained earlier, physical properties, including tensile properties, are closely related with the diluent monomers (Ali et al. 1998). Several types of instruments are available for determining tensile properties. Horizontal tensile loading tester is used for tensile experiments. The sample is mounted between two jaws of the tester; care must be taken to ensure that the film is in line with the direction of pull. The interrelationships of ideal elasticity can be described by Hooke's law between the tensile force F acting on a body in the case of elongation and the resultant deformation (Goldschmidt and Streitberger

Table 3. ARUA pendulum hardness results.

Conveyor speed (m/min)	Obtained sample	Pendulum hardness (könig)
3.0	*Free film*	22
2.0	*Free film*	23
1.0	*Free film*	24
0.1	*Free film*	26
3.0	*Coated CPS*	14
2.0	*Coated CPS*	16
1.0	*Coated CPS*	17
0.1	*Coated CPS*	18
-	*Untreated CPS*	8

Table 4. ALUA pendulum hardness results.

Conveyor speed (m/min)	Obtained sample	Pendulum hardness (könig)
3.0	*Free film*	13
2.0	*Free film*	14
1.0	*Free film*	16
0.1	*Free film*	19
3.0	*Coated CPS*	9
2.0	*Coated CPS*	11
1.0	*Coated CPS*	12
0.1	*Coated CPS*	14
-	*Untreated CPS*	8

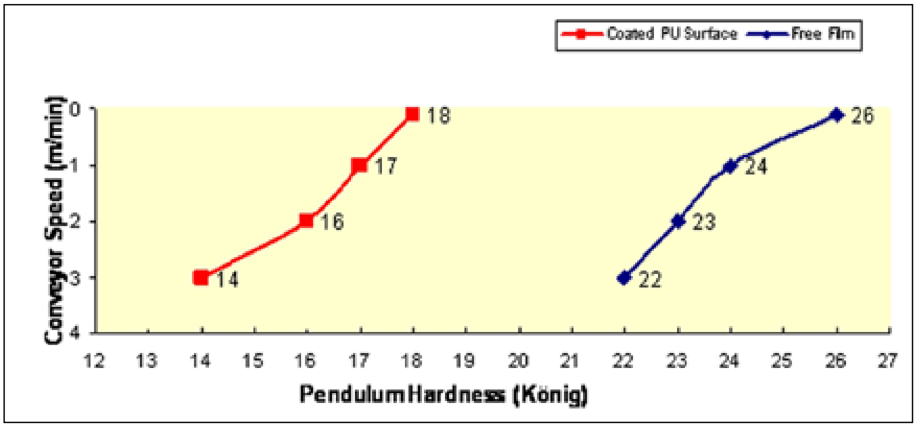


Figure 6. ARUA pendulum hardness graph.

2003, Wicks et al. 2007). Specimens for tensile testing are carefully cut in the shape of a dumbell as described EN ISO 527-3.

3. Results and Discussion

In this study, aromatic and aliphatic urethane acrylate oligomer formulations are prepared. Both formulations consist of high molecular weight viscous oligomer, mono and multi acrylic functional reactive diluents, polysiloxane and photoinitiator. Those two different formulations are coated on both Al plates and coagulated polyurethane (CPS) surfaces and cured by means of ultraviolet (UV) radiation. After curing with different conveyor speeds obtained samples are subjected to further physical and mechanical tests. König pendulum hardness tests are applied after ARUA and ALUA coated Al plate and CPS samples are UV cured with different conveyor speeds from 0.1 m/min to 3.0 m/min. Tests were applied while the cured film was still on coated CPS and after cured film was peeled off Al plates. The results are given at Table 3 and Table 4 and related graphs are shown at Figure 6 and Figure 7.

As it is seen at Figure 6 and Figure 7 for both ARUA and ALUA applications; pendulum hardnesses of samples have increased with decreasing conveyor speed which means as curing increases pendulum hardnesses of surfaces have inreased with both of the treatments. The gel content is a representation of crosslinking density in the cured film as a whole, determined by soxhlet extraction. The gel contents of the UV-cured free films prepared from ARUA and ALUA formulations are shown at Table 5.

Gel content results given in Table 5 confirms that in very short time polymerization rates are very high in UV curing in comparison to conventional polymerization. In addition to that gel content, crosslinking density, has increased slightly with decreasing conveyor speeds (longer cure time).

Table 5. Gel contents for ARUA and ALUA.

Conveyor speed (m/min)	3.0	2.0	1.0	0.1
Gel content of ARUA	95.7 %	95.8 %	95.9 %	96.0 %
Gel content of ALUA	98.6 %	98.8 %	98.9 %	99.0 %

Table 6. Swelling ratios of ARUA and ALUA.

Conveyor Speed (m/min)	3.0	2.0	1.0	0.1
Swell ratio of ARUA samples	50.8 %	46.0 %	43.5 %	34.4 %
Swell ratio of ALUA samples	30.2 %	27.3 %	23.0 %	21.0 %

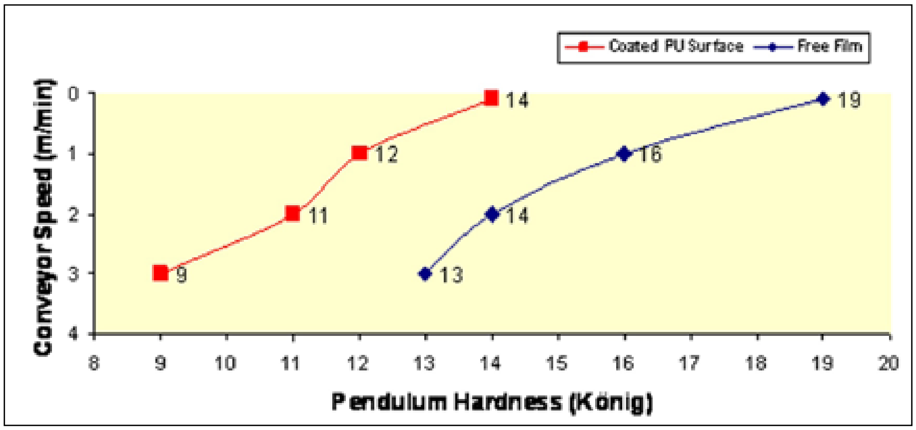


Figure 7. ALUA pendulum hardness graph.

Gel content results of ARUA formulations were lower than of ALUA. This can be due to free volume effect of chromophoric groups. In ARUA, aromatic groups prevent dense(frequent) crosslinking; while in ALUA crosslinking is denser. Swelling ratios of free films were determined by acetone solvent. The resulting swelling ratios of free films given in Table 6 prove that with decreasing conveyor speed, solvent swelling (swell ratios) decreases. This can be due to crosslinking density increase with increasing curing time.

Swell Ratios of ARUA Samples are higher in comparison to ALUA samples. This result is related to gel contents; crosslinking densities. The reason for this is probably ARUA; as it has aromatic groups (its crosslinking density lower); has much more free volume; as a result its solvent penetration is easier than ALUA; which has higher crosslinking densities.

Water uptake test are performed to monitor water resistance of samples. Water absorption of untreated and treated CPS samples were determined in Table 7.

Table 7 depicts ALUA and ARUA treated CPS samples approximately 100 times more water resistant than untreated CPS sample. Reflectance values and wavelengths of ALUA and ARUA treated and untreated CPS samples are obtained from the spectrophotometer data. The results obtained are given in Table 8 and the graph indicating reflectance(%) values vs. wavelength is shown at Figure 8.

Table 8 and Figure 8 shows the reflactance results of ARUA and ALUA treated and untreated CPS samples. Here, the results are surface reflectivity values at the illumination of 440 nm, 465 nm, 546 nm, 590 nm, 635 nm wavelengths which means color violet, blue, green, yellow and red respectively. As shown in Figure 8 reflectance (R %) values at same wavelengths have decreased with decreasing conveyor speeds for ALUA treated CPS samples; while values tend to increase with decreasing conveyor speeds for ARUA treated CPS samples. ARUA samples composed of aromatic groups, tend to degrade with increasing UV exposure. This may be due to degradation of ARUA with increasing cure time, as sample was exposed to UV light longer time.

Tensile properties are very important in selecting diverse applications of polymer and polymer-coated substrates (Khabir Uddin et al. 1996). Tensile properties may be utilized to provide data for research and development and engineering design as well as quality control and specification. Tensile properties may vary with specimen thickness, method of preparation, speed of testing, type of grips used and manner od measuring extension (Ha et al. 1996).

Table 7. Water uptake (%) ratios.

Sample	Water Uptake (%) in 5 min.
CPS (untreated)	10.00 %
ARUA treated (3.0)	0.03 %
ARUA treated (2.0)	0.05 %
ARUA treated (1.0)	0.07 %
ARUA treated (0.1)	0.04 %
ALUA treated (3.0)	0.03 %
ALUA treated (2.0)	0.02 %
ALUA treated (1.0)	0.04 %
ALUA treated (0.1)	0.02 %

The results are given in Table 9 and related graphs are shown in Figure 9 and Figure 10.

Tensile test results in Figure 9 and Figure 10 show the tensile strength of all treated samples. Treated CPS samples tensile strengths increased in comparison to untreated CPS sample; meanwhile maximum strain(%) decreased. Both with ALUA and ARUA coating, the mechanical properties of CPS material is enhanced by treatment. On the other hand, it seems, with ALUA coating had attained better results in order to use this treated CPS material as a synthetic leather in shoe and luggage industry.

4. Conclusion

Crosslinking densities of cured films have increased with increasing exposure time to UV light. As a result of this, pendulum hardnesses, gel contents, water resistance of treated samples have increased while their swelling ratios are satisfactorily decreased. Crosslinking densities, and

Table 8. Spectrophometer data.

Sample	R% (440 nm)	%R (465 nm)	%R (546 nm)	%R (590 nm)	%R (635 nm)
Untreated CPS	58.131	70.3974	88.1855	91.5537	92.901
ALUA(3.0)	41.9515	54.7534	73.2513	76.5751	77.9302
ALUA(2.0)	39.1531	51.0181	67.7302	70.4924	71.6198
ALUA(1.0)	34.917	44.563	57.8191	60.0343	60.9756
ALUA(0.1)	21.5556	32.7499	52.3622	54.286	55.974
ARUA(3.0)	17.7783	29.1053	45.7704	49.7086	50.057
ARUA(2.0)	28.1666	37.4396	50.5182	52.8035	53.9056
ARUA(1.0)	29.4355	39.0127	52.0647	54.2425	55.3391
ARUA(0.1)	30.5678	40.8713	54.9389	57.1832	58.1822

Table 9. Tensile properties of untreated and treated samples.

Sample (CPS)	Tensile Strength (N/mm^2)	Max. Strain (%)	Elastic Modulus (N/mm^2)
ALUA(3.0)	11.70	23.33	0.40
ALUA(2.0)	13.10	16.66	0.79
ALUA(1.0)	11.40	13.33	0.90
ALUA(0.1)	11.00	13.33	0.88
ARUA(3.0)	9.40	16.66	0.55
ARUA(2.0)	12.60	20.00	0.71
ARUA(1.0)	7.00	23.33	0.82
ARUA(0.1)	9.70	13.33	0.70
Untreated sample	7.90	33.33	0.23

gel contents of ALUA were higher than ARUA while pendulum hardnesses (at surface) and swell ratios are higher with ARUA coatings. This may be due to free volume effect of aromatic groups in ARUA coating. Physical behaviour of treated CPS samples are determined by spectrophotometry. ARUA coated materials tend to degrade with longer UV exposure time. Tensile tests are applied to CPS samples. Elongation of treated sample have decreased in comparision to untreated CPS sample; while tensile stress at break and young's modulus values have increased. All the treated CPS samples have attained the enhanced strength**.** The best properties obtained seems to be with the ALUA CPS sample UV cured at 8 pass at 2.0 m/min conveyor speed. By coating CPS with ALUA and ARUA formulations via UV radiation, the material have been acquired desired mechanical properties. This observation is currently under further investigation.

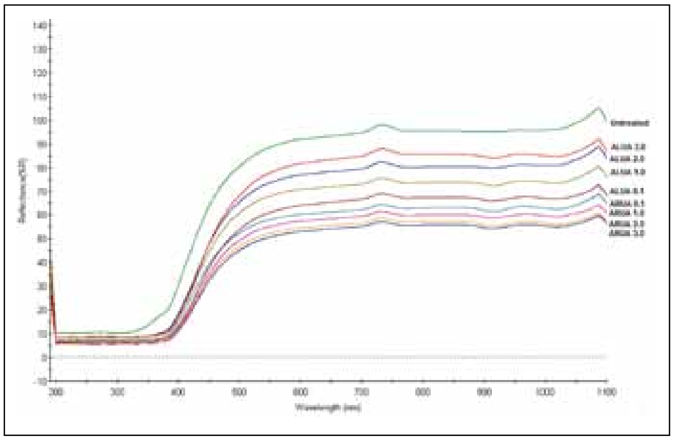


Figure 8. Reflectances of ALUA and ARUA samples.

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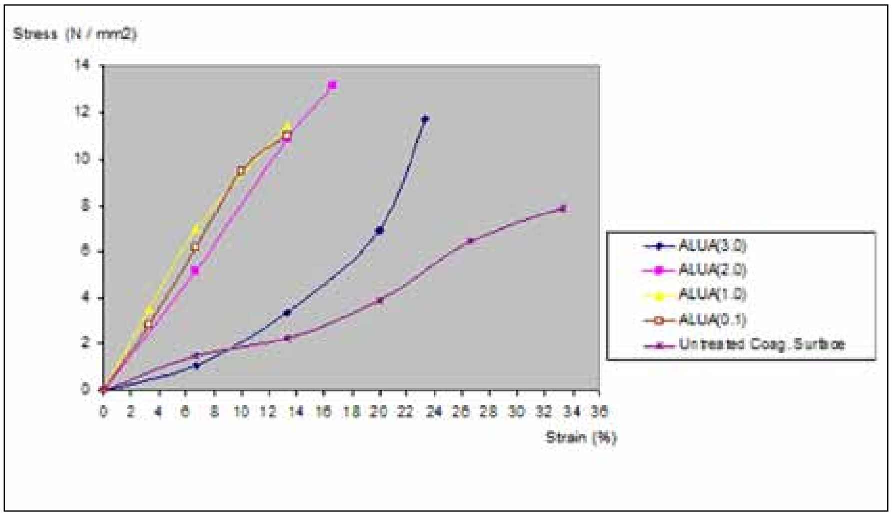

Figure 9. ALUA treated CPS samples stress strain graph.

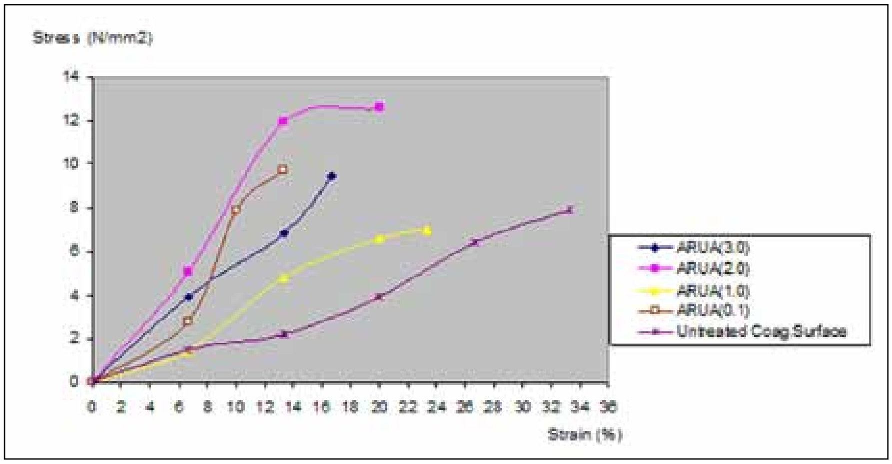

Figure 10. ARUA treated CPS samples stress strain graph.

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