

Photocuring of Acrylate Oligomers in the Presence of Vinyl Phosphonic Acids as a Flame Retarding Monomer and the Properties of the Cured Films

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Photocuring of formulations containing polyurethane based acrylates and a flame retarding monomer (FR), namely vinyl phosphonic acid with an α -cleavage type photoinitiator; 2-hydroxy-2-methylphenyl propane-1-one were studied. The flame retardancy, and the physical and mechanical properties of the cured films were determined.

Key Words: Flame retardancy, U.V. curable polyurethane acrylate, vinyl phosphonic acid.

Introduction

There has been considerable interest in the application of coating systems in various fields. Some of these systems are based on U.V. induced polymerizations where either of the bifunctional acrylate or epoxy monomers undergo crosslinking by radical or cationic mechanisms, respectively¹. For indoor or outdoor uses of such materials, it is necessary to protect them from fire. The nonflammability of U.V. cured coatings has therefore been a longstanding requirement.

In earlier investigations for reducing the flammability of polymeric materials, large amounts of metal hydroxide, halogenated, phosphorous-, nitrogen- and sulfur-containing compounds were usually added to coatings as flame retardants (FR). However, the addition of a large amount of additive will result in changes in the mechanical properties of the U.V. cured coatings. The incident light may be absorbed by the additives and thus curing efficiency is reduced. Additionally, additives may separate out from the polymer after curing due to incompatibility.

One way to overcome these drawbacks is to employ a reactive monomer possessing flame retarding properties in the formulation. Thus, flame retarding sequences will be part of the final product as a result of their participation in the related polymerization through the olefinic bond existing in the monomer². In a previous work, we have described the use of a FR monomer, pentabromobenzyl acrylate, together with polyester and polyurethane based acrylates in U.V. curable free radical formulations³. Efficient curing was achieved by using various α -cleavage type photoinitiators. The flame retardancy, which was accomplished by the evolution of hydrogen bromide and thus preventing oxygen penetration, was quite satisfactory⁴.

However, hydrogen bromide itself is hazardous and can cause even more severe results in the event of fire. We have, therefore, switched our interest to the use of a phosphorous containing monomer, vinyl phosphonic acid, in the corresponding formulations. As shown below, by the use of this monomer, flame retardancy is achieved during burning and no hazardous gas is evolved.

Experimental

Materials: 2-hydroxy-2-methyl-phenyl propane-1-one (Daracure 1173)(CIBA, Speciality Chemicals), vinyl phosphonic acid (VPA) (Aldrich Chem. Co.), N-vinyl pyrrolidone (NVP)(BASF), 1,6-hexandioldiacrylate (HDDA) (UCB), Trimethylol-propane triacrylate (TMPTA)(UCB), Aromatic urethane triacrylate (containing 25% HDDA)(UCB), isotridecyl alcohol 6 ethoxylate (ITDA-6EO)(Condea), phosphorous pentoxide (Clariant) and acetone (Merck) were commercial grade products and used as purchased.

Preparation and UV Curing of Coating: The formulations, tared and then mixed with a mechanical stirrer, were coated onto polished glass plates (5×10 cm) with the help of a four-sided stainless-steel bar coater, which gave 120 μm thick films. The samples were irradiated for given times from a photoreactor consisting of 8 Phillips TL6W/08/F6T5 BLB type U.V. lamps. Irradiation distance was 30 cm. Retardation due to the scavenging effect of oxygen was ignored in this study.

Analyses

Gel Content Determination: The resins after photocuring were extracted by acetone at 60°C for 48 h and residual polymers were dried and weighed.

Gloss Measurement: Gloss measurement was performed with a Novo-Glossmeter at different angles on cured films.

Tensile Strength Analyses: Cured films were cut into 50 × 200 mm strips. After conditioning for 2 h at 23°C/65% humidity, the specimen was tested with a Zwicki 1120 Testing Machine.

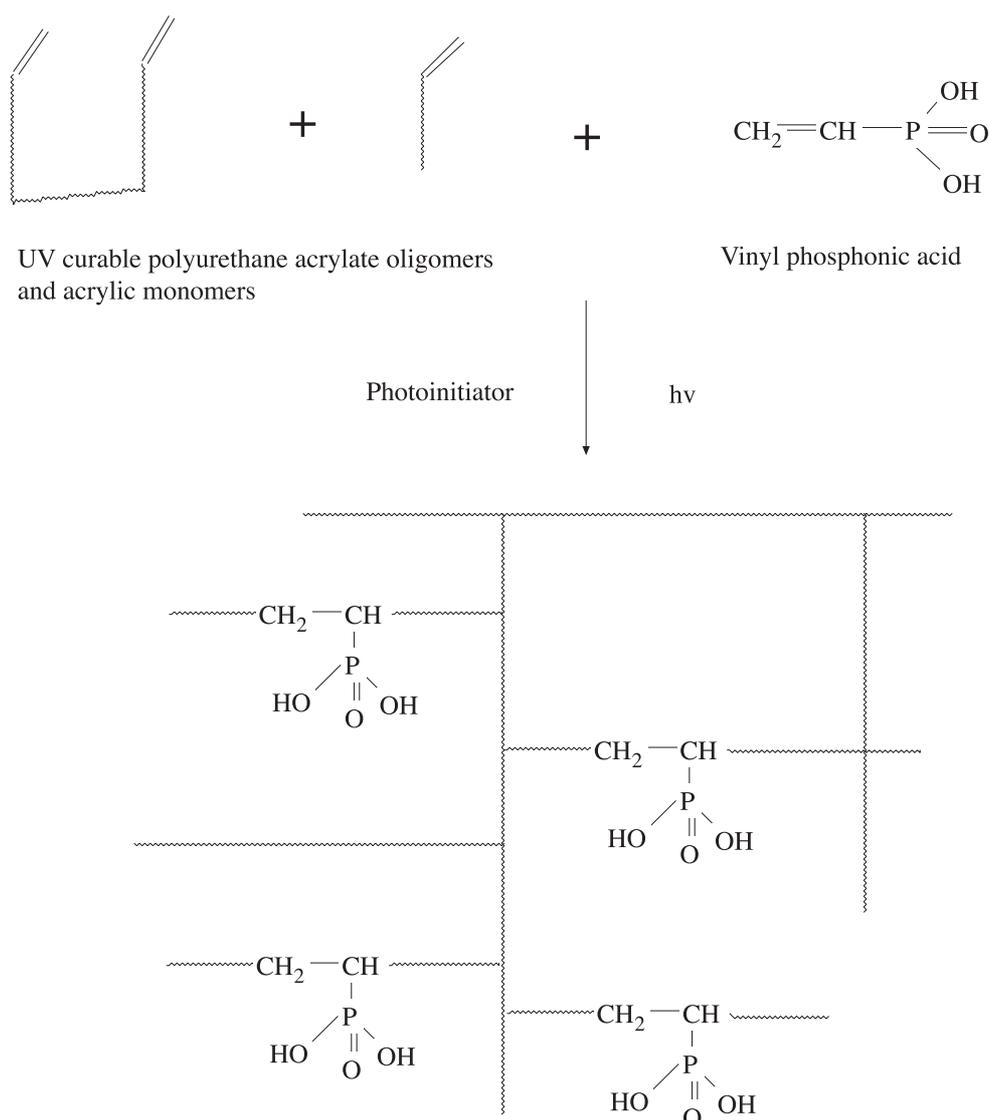
Thermogravimetry Analyses: Thermogravimetry analyses were carried out on a Shimadzu TG 50 Thermogravimetric Analyzer, by using air as the carrier gas. About 10 mg of each sample was heated at a rate of 20°C/min over a temperature ranging from room temperature up to 800°C.

Limiting Oxygen Index: Oxygen index testing device was built up in house, according to the ANSI/ASTM D2863-77 method. In this method, the limiting oxygen index (LOI) is defined as the minimum concentration of oxygen in a flowing mixture of oxygen and nitrogen that supports candle-like combustion of a specimen. According to the standard method, five test specimens with about 0.3 mm thickness, 5 mm width, and 140 mm length were cut from the cured polymer film. Flaming of the specimen past the 100 mm reference mark was judged to meet the criterion of burning⁵.

Ash Content Determination: The samples were tared carefully and burned for 2 h in an 800°C oven. The residual ash tared and ash content were calculated as percentages.

Results and Discussion

The photoinitiator used in this study is an α -cleavage type initiator and upon photolysis produces two radicals capable of reacting with the olefinic components of the resins to yield an insoluble network. Thus an FR monomer was incorporated into the network by chemical bonding (Scheme 1).



Scheme 1. Photocuring mechanism of VPA monomer with polyurethane acrylate resin.

The typical formulations used in this study contain 60% urethane acrylate oligomer, 10% TMPTA, 15% HDDA, 10% NVP and 5% photoinitiator by weight⁶. The urethane acrylate FR resins were then prepared by replacing monofunctional monomer NVP with FR monomer VPA in increasing amounts.

The determinations of tensile strength and elongation of the cured films containing various amounts of VPA provide additional information about the specific influence of FR monomer on the mechanical properties^{7–11}. Addition of VPA in the range of 1 to 9% resulted in some improvement in tensile strength and elongation (Table 1). The partial replacement of more rigid N-vinyl pyrrolidone by FR monomer in the corresponding polyurethane-based network causes an increase in the tensile strength¹². Additionally, as the amount of VPA monomer increases, the hydrogen bonding and dipole interactions between chains are reduced due to the hygroscopic property of the VPA monomer¹³. Therefore, polymer chains gain greater mobility and thus elongation at break increases. The variations in the tensile properties also depended on the gel content and the type and percentage of crystalline formation in the network.

In studies on flame retardancy by means of LOI and TGA, destruction of the UV cured films containing FR monomer sequences gives valuable information about their burning¹⁴. As seen in Figure 1, the thermal stability of cured films is affected by the substitution of FR monomer. Increasing the amount of FR monomer increases the residual content. This is also detectable as an increase in ash content values, which are given in Table 2. The mechanism in which combustion of the outer layers of the polymeric resin containing FR monomer leads to the production of an intumescent carbonaceous char through the formation of transient, intermolecular anhydride links (see Scheme 2). The char acts as physical and thermal barrier to further combustion by impeding heat transfer to the underlying layers of virgin polymer and thus prevent the release of further flammable volatiles¹⁵ (Scheme 3).

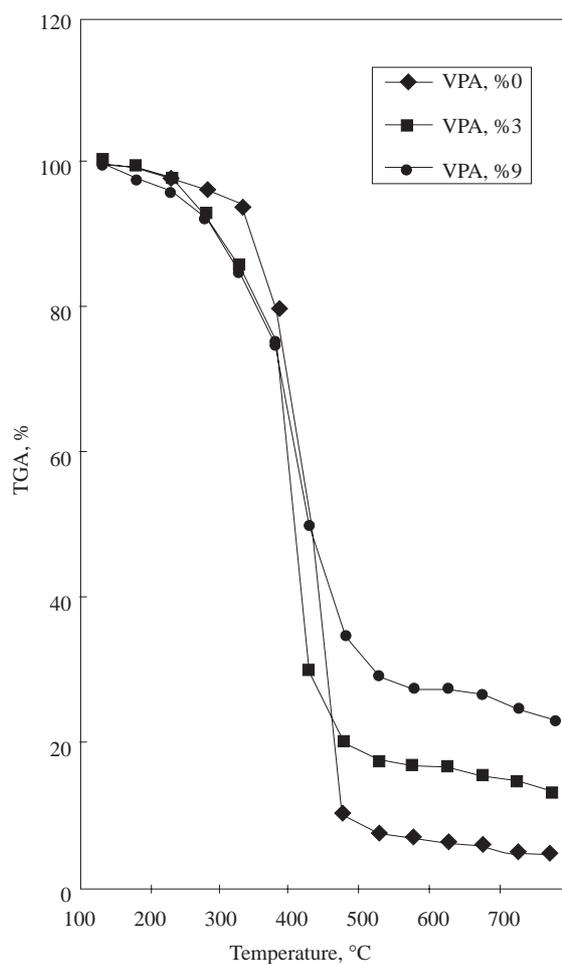
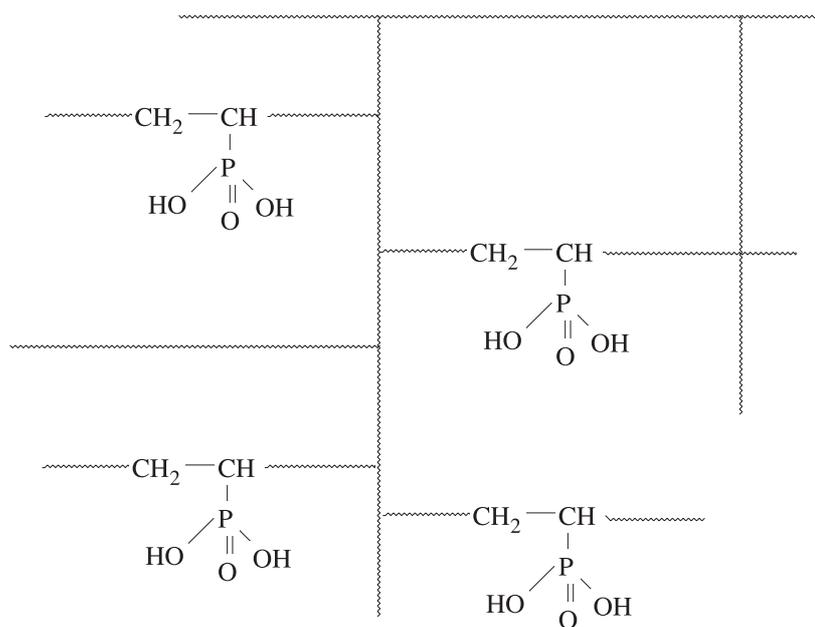
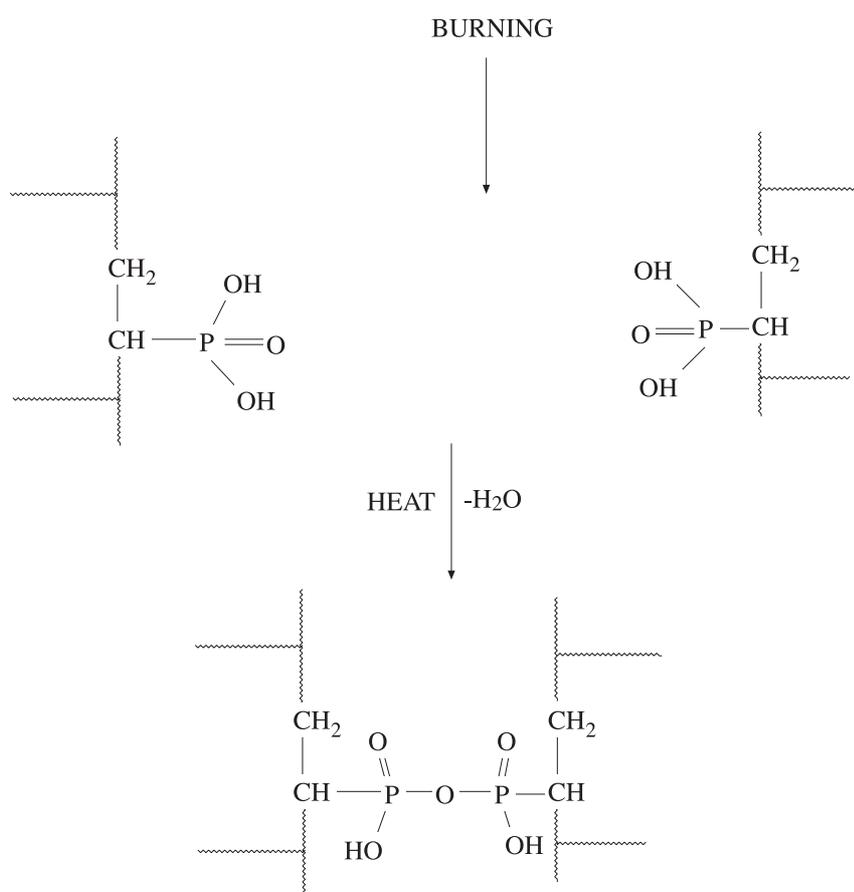


Figure 1. TGA thermograms of cured polyurethane based resins with FR monomer.

LOI analyses were also performed on the same samples of cured resins. It is known that LOI is related with FR monomer concentration and has a linear relationship with the crosslinking density and consequently with the gel content. The oxygen demand to burn the cured resin increases respectively with increasing amounts of FR monomers in the formulation. The accepted limit of the oxygen index for covering the self-extinguish definition of polymers is 26%¹⁵. From these experimental results, it is revealed that 1% VPA monomer in a urethane acrylate based system is sufficient to reduce the flammability characteristics of cured resins.



Polyurethane-based resin with vinyl phosphonic acid monomer



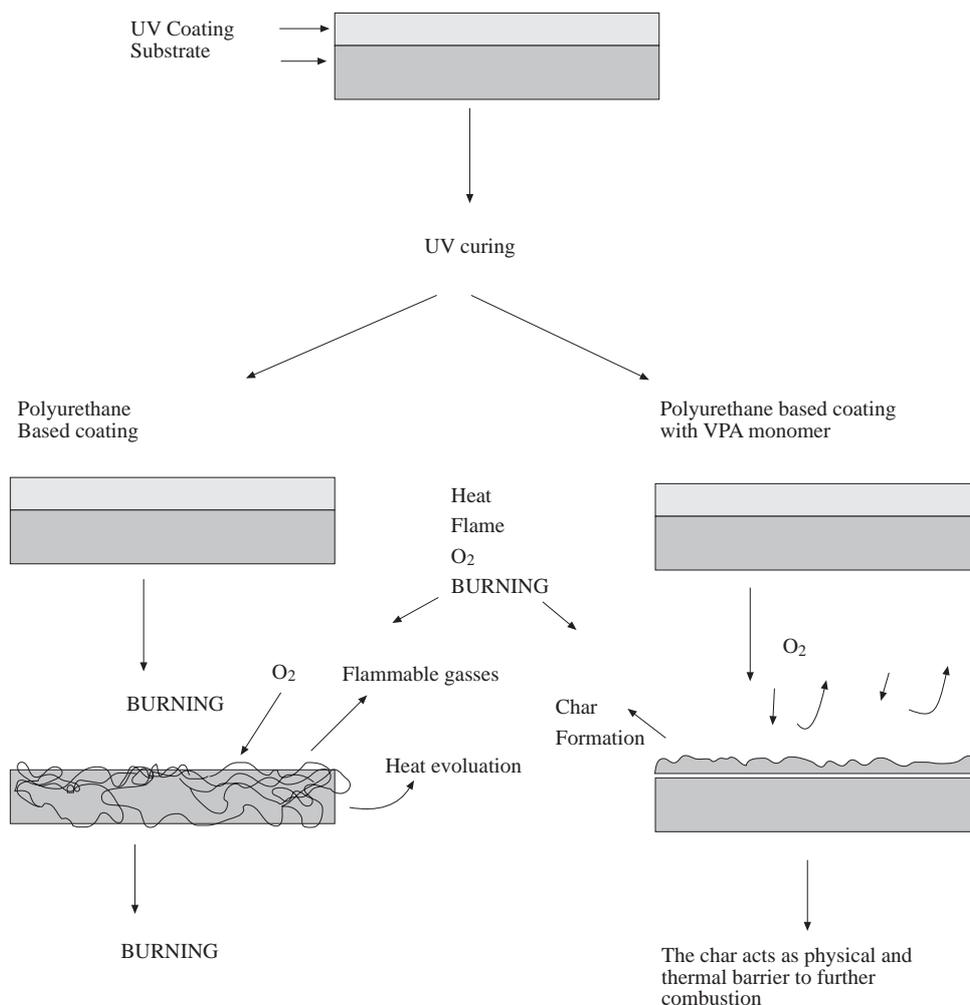
Scheme 2. Possible mechanism of crosslinking leading to char formation.

Table 1. Mechanical and physical properties of UV cured films of unsaturated polyurethane based resins containing FR monomer.

VPA %	0	1	3	5	9
Gel content	95.8	82.5	84.3	84.2	84.6
Gloss 60'	146	108.7	79.2	64.7	88.5
Elongation %	5.2	58	43.	4 40	39.2
Tensile Strength, KPa	187	1078	1006	1032	1107

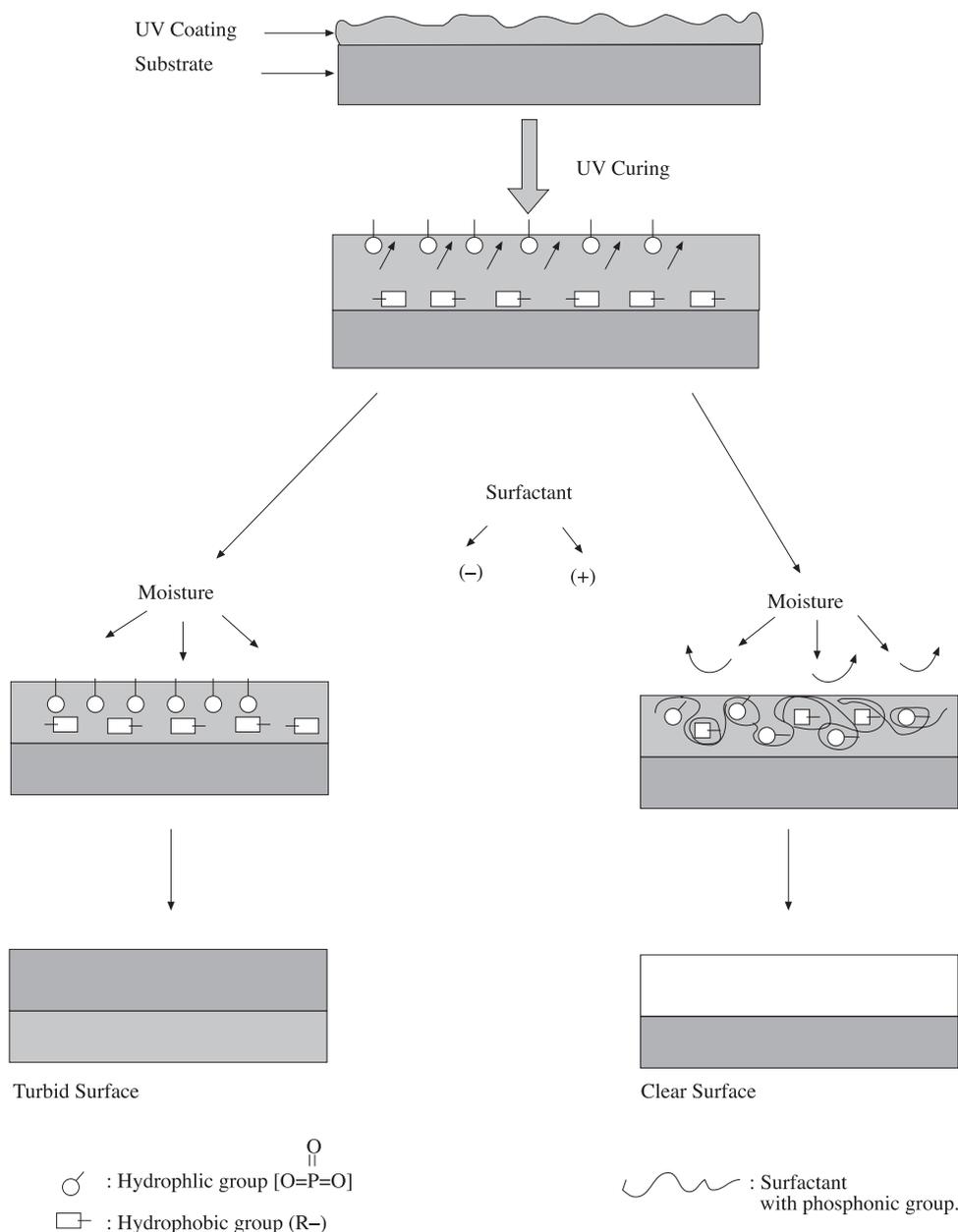
Table 2. The Limiting Oxygen Index (LOI) values and the ash contents of the UV cured films of a polyurethane-based system containing various amounts of FR monomer.

VPA %	0	1	3	5	9
LOI, %	17	42	76	>100	>100
Ash, %	0	0.14	0.26	0.69	1.33



Scheme 3. Flame retarding mechanism of VPA monomer in polyurethane acrylate based films and coatings.

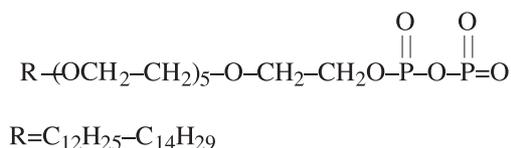
It is obvious that flame retardant polyurethane-based resins could be prepared by introducing VPA monomer and cured photochemically without causing any unfavorable effects in the mechanical properties. However, there were visually detectable changes on the surface of cured resins. The clear films were converted into turbid surfaces within 24 h of curing. This is also observed from the decrease in gloss levels of cured films. The gloss decreases with increasing amount of the VPA monomer. The detrimental effect of VPA monomer could be explained by migration of hydrophilic phosphonic acid groups toward the surface and absorbing humidity on the surface of the cured film (Scheme 4).



Scheme 4. The effect of moisture on polyurethane acrylate based coating with VPA monomer.

To prevent the migration of vinyl phosphonic groups, a long chain surfactant molecule containing phosphoric groups was designed. The phosphonic groups of the molecule acts as the compatibilizer for the

vinyl phosphonic acid component. The encapsulated and distributed vinyl phosphonic groups are therefore expected not to be able to come into contact with humidity. For this purpose, 2.5 mole isotridecyl alcohol-6 ethoxylate was introduced partially and slowly on 1 mole phosphorous pentoxide in a vessel placed in an ice bath. The reagents were mixed well for 30 minutes and the final mixture was used without any purification. The synthesized surfactant of the following structure was introduced to the polyurethane oligomer based resin in the presence of VPA monomer. The results are given in Table 3.



As clearly seen in Table 3, the introduction of a phosphonic type surfactant molecule to the system could result in the formation of clear films. Although there are some changes in mechanical properties of the cured films, it is possible to arrange characteristics of the film by selecting appropriate oligomers and monomers in combination with a suitable surfactant such as the one described here.

Table 3. Mechanical and physical properties of UV cured films of unsaturated polyurethane based resin containing VPA monomer and the surfactant.

VPA, %	1.5	2.25
Surfactant, %	0	1
Appearance ^a	Turbid	Clear
Gel Content, %	84.42	83.20
Tensile Strength (KPA)	1053	992
Elongation, %	55.3	43
LOI, %	47	78

^a Appearance of films within 24 h of curing.

In conclusion, PU based UV curable coatings containing a FR monomer, namely VPA monomer, can be prepared and cured by irradiation in the presence of a radical photoinitiator. The resulting polymers in general have higher LOI values than those of the untreated ones.

Acknowledgements

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